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INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
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"Inelastic Energy Transfer in Vibrational Spectroscopy of Adsorbates"

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Inelastic Energy Transfer in Vibrational Spectroscopy of Adsorbates.

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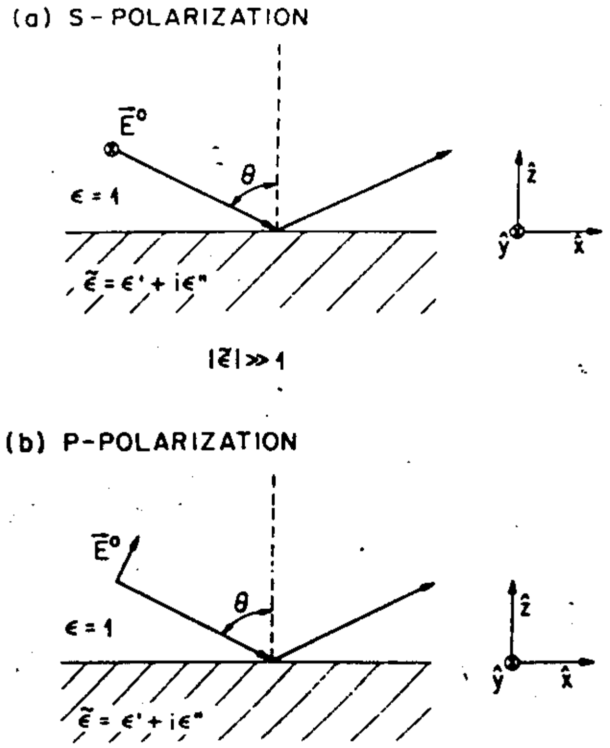
Inelastic Energy Transfer in Vibration Spectroscopy of Adsorbates.

Contents

LIST OF SURFACE VIBRATIONAL SPECTROSCOPIES

1. Electron energy loss spectroscopy (EELS)
2. Surface infrared spectroscopy (SIRS)
3. Surface Raman scattering
4. Inelastic atom beam scattering
5. Inelastic electron tunneling spectroscopy
6. Inelastic neutron scattering



ig. 2. Schematic representation of a plane wave beam of radiation incident at an angle θ onto a etallic or strongly absorbing substrate for the two polarizations of interest. Note that the symbol sed to represent E in (a) [and $\hat{y}$ in both (a) and (b)] indicates a vector pointing into the plane of the figure.

SELECTION RULE:

Only vibrational modes that have a dipole moment normal to the surface are most favourably excited in IRAS

The selection rule does not stricly fulfiled in IRAS

Vibrational lineshape: Basic principles

Reflectance for p-polarized beam

$$\frac{\Delta R}{R} = -\frac{16\pi\omega}{\cos\theta\, c}\, \mathrm{Im}\left[\alpha_\perp \sin^2\theta - \frac{\alpha_\parallel}{\epsilon}\right]$$

Polarizability

$$\alpha(\omega) = -i\int_0^\infty \exp(i\omega t)\langle[\hat{p}(t)\,\hat{p}(0)]\rangle dt$$

If $\langle p(t)\,p(0)\rangle \sim \exp\left[-i(\omega_0+\Delta\omega)t - \frac{\Gamma}{2}|t|\right]$

Then the lineshape

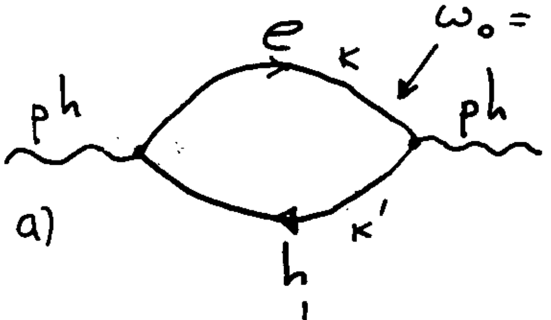
$$L(\omega) \sim \mathrm{Re}\int_{-\infty}^{\infty} e^{i\omega t}\langle p(t)\,p(0)\rangle dt =$$

$$= \frac{\Gamma/2}{(\omega-\Delta\omega-\omega_0)^2+(\Gamma/2)^2}$$

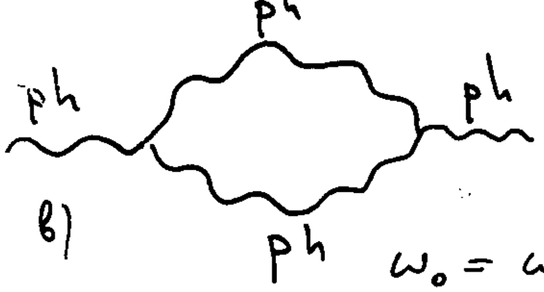
3. ENERGY TRANSFER ACCOMPANYING VIBRATIONS OF ADSORBATES

In a vacuum the damping of the vibrations of a molecule occurs by means of a single mechanism—the radiation mechanism (with emission of a photon), for which, as is well known, $\tau^{-1} \approx \mu^2(\omega_0/c)^3$. On adsorption the lifetime of the vibrations decreases by many orders of magnitude; this indicates that the main mechanisms for the damping of the vibrations in this case are associated with excitation of quasiparticles of the substrate—phonons, electron-hole pairs, plasmons, etc. If the frequency of the vibrations of the molecules $\omega_0 > \omega_m$, where ω_m is the maximum frequency of the vibrational spectrum of the substrate, then damping of the vibrations of the admolecule owing to excitation of phonons is possible only owing to the anharmonicity of the vibrations. The electron-hole pairs are generated in the process of inelastic scattering of conduction electrons by the oscillating potential of a molecule. This potential can be separated into short- and long-range parts. The mechanism of damping associated with scattering by the short-range potential is simply called electron-hole damping. This mechanism can play the main role in chemisorption. Scattering of electrons by the long-range potential leads to the electromagnetic mechanism of damping, which plays an important role in physical adsorption. For metals the plasmon frequency is $\omega_p \gg \omega_0$, so that the plasmon mechanism of damping is inefficient fo. adsorption on metals. This mechanism can, however, be efficient for adsorption on semiconductors, for which it can happen that $\omega_p \approx \omega_0$.

$\omega_0 = \varepsilon_K - \varepsilon_{K'}; \quad \varepsilon_K > \varepsilon_F, \quad \varepsilon_F' < \varepsilon_F$

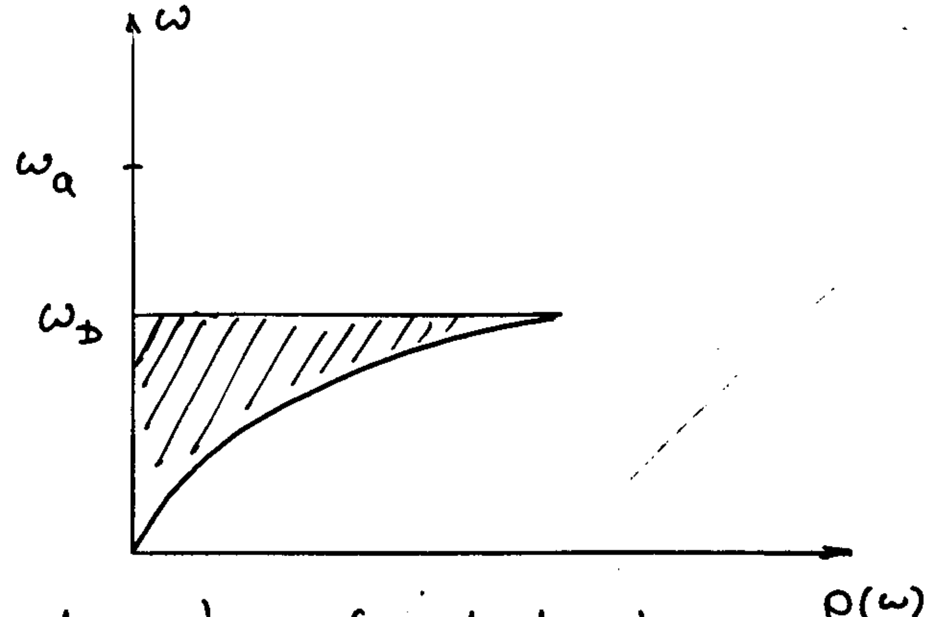


electron-hole mechanism

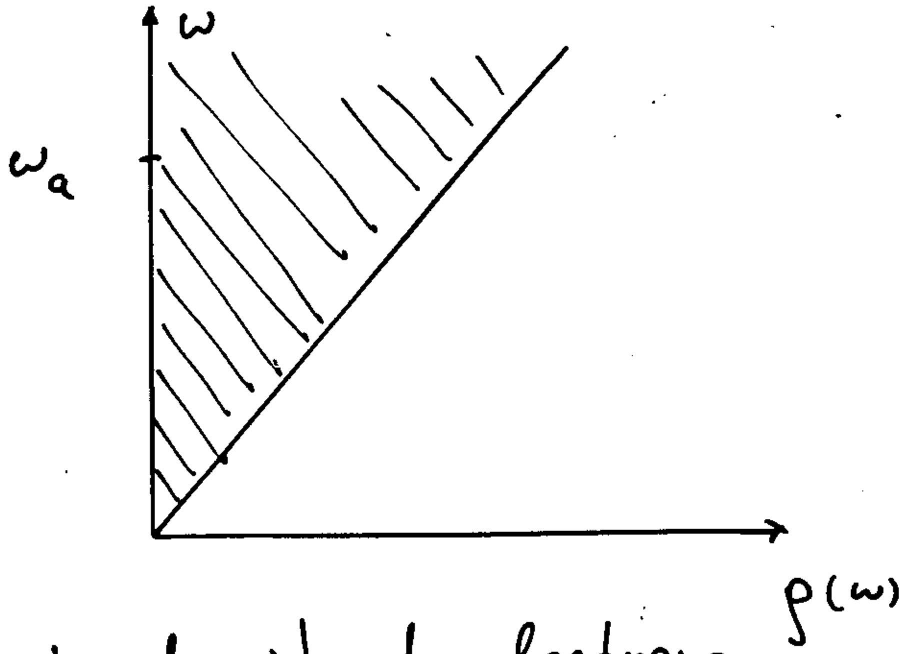


phonon mechanism

$\omega_0 = \omega_1 + \omega_2$



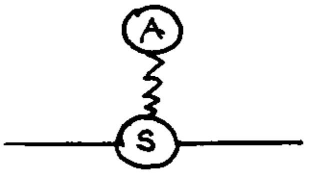
the density of substrate phonon states



the density of electron-hole pair states

Phonon mechanism of vibrational energy transfer.

$$H_{anharm} = H_{harm} + H_{int}$$



adatom in the top position

$$V(z_a - z_s) = D\{\exp[-2\alpha(z_a - z_s)] - 2\exp[-\alpha(z_a - z_s)]\}$$

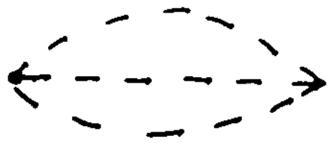
$$H_{int} = \lambda_3 q^3 + \lambda_4 q^4 + \dots$$

$$q = z_a - z_s$$

a)

q^3

b)



q^4

c)

q^3

Linewidth due to multiphonon processes

$$\Gamma = \frac{g \pi \omega_a}{16 D}\left(\frac{m_a}{M}\right)\frac{\omega_a K}{1 + n(\omega_a)}$$

$$K = \sum_{n=0}^{\infty}\left(\frac{g \cdot m_a \omega_a}{16 M_s D}\right)^n \frac{1}{n!}\int d\omega_1 \cdots \int d\omega_{n+1} \times$$

$$\times \frac{\omega_a^{3n+3}(1+n(\omega_1))\cdots(1+n(\omega_a-\omega_1-\cdots\omega_{n+1}))}{\omega_1^3\,\omega_n^3\,\omega_{n+1}(\omega_a-\omega_1-\cdots-\omega_{n+1})} \times$$

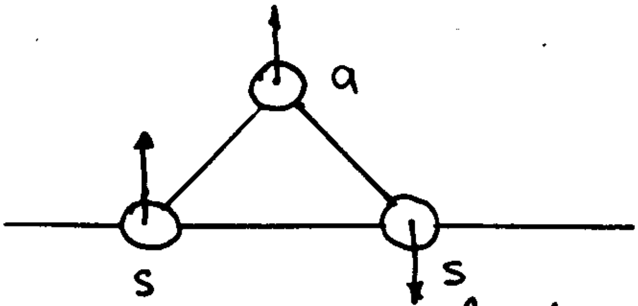
$$\times\ \rho(\omega_1)\cdots\ \rho(\omega_a-\omega_1-\cdots-\omega_{n+1}).$$

$$\rho(\omega) = \frac{\omega^4}{(\omega^2-\omega_a^2)^2}\,\rho^{bare}(\omega)$$

↗ reduction factor.

Conclusion: All perpendicularly modes can be neglected when discussing anharmonicity for molecule bound in the top position.

D. Langreth, M. Persson, 1991
B. N. J. Persson, 1989
Reduction factor absents for molecule bound in the bridge position



adatom in the bridge position

3.2. The electromagnetic mechanism. If a molecule is physically adsorbed or is located quite far from the surface of the metal, the electric field from the oscillating dipole of the molecule penetrates into the bulk of the metal, and this generates electron-hole pairs. The Hamiltonian for the interaction of the vibrations of the molecule and the electrons of the metal has the form

$$H_{\rm int} = Q_{\rm A}\int g(\mathbf{r})\,\hat{\rho}(\mathbf{r})\,d^3\mathbf{r}, \qquad (3.21')$$

where $Q_{\rm A}$ is the normal coordinate of the vibrations, $Q_{\rm A}g(\mathbf{r})$ is the change in the potential energy of the molecule accompanying a displacement of the normal coordinate from the position of the equilibrium by an amount $Q^{o}_{\rm A}$, and $\hat{\rho}(\mathbf{r})$ is the electron density operator for the metal. In the linear-response approximation the polarization operator can be represented in the form

$$\Pi(\omega) = \int d^3\mathbf{r}' \int d^3\mathbf{r}\,\varphi(\mathbf{r})\,\chi(z, z', \mathbf{x}-\mathbf{x}', \omega)\,\varphi(\mathbf{r}'), \qquad (3.23)$$

where $\varphi(\mathbf{r})$ is the potential of a point dipole with the dipole moment

$$\mu = e^{*}Q_{0} = e^{*}(2m\omega_{0})^{-1/2}.$$

The charge-density response function for a semiinfinite metal $[\mathbf{r} = (\mathbf{x}, z)$; the metal is assumed to occupy the half-space $z<0]$ is given by the formula

$$\chi(z, z', \mathbf{x}-\mathbf{x}', \omega) = -i\int_0^{\infty} \exp(i\omega t)\,\langle[\hat{\rho}(\mathbf{r}, t),\ \hat{\rho}(\mathbf{r}', 0)\rangle\,dt. \qquad (3.24)$$

Introducing the function

$$g(q_{\parallel}, \omega) = \frac{2\pi}{q_{\parallel}}\int dz \int dz' \exp[q_{\parallel}(z+z')]\,\chi(z, z', \mathbf{q}_{\parallel}, \omega), \qquad (3.25)$$

where

$$\chi(z, z', \mathbf{q}_{\parallel}, \omega) = \int \exp(i\,\mathbf{q}_{\parallel}\mathbf{x})\,\chi(z, z', \mathbf{x}, \omega)\,d^2\mathbf{x}, \qquad (3.26)$$

and carrying out the two-dimensional Fourier transform in the integrand in (3.23) gives[27,28]

$$\boxed{\Pi(\omega) = \left(\frac{\mu_{\parallel}^2}{2} + \mu_{\perp}^2\right)\cdot\frac{1}{2}\int_0^{\infty} q_{\parallel}^2 \exp(-2q_{\parallel}d)\,g(q_{\parallel}, \omega)\,dq_{\parallel},} \qquad (3.27)$$

. If spatial dispersion is neglected, i.e., the metal is described by a local permittivity, equal to the bulk value of $\varepsilon(\omega)$ for $z<0$ and unity for $z>0$, then the response function can be expressed in terms of the permittivity[36]

$$g(q_{\parallel},\ \omega)=(\varepsilon(\omega)-1)(\varepsilon(\omega)+1)^{-1}. \tag{3.28}$$

In Drude's approximation $\boxed{\varepsilon(\omega)=1-[\omega_p^2/\omega(\omega+i\tau)],}$ where ω_p is the bulk plasma frequency, $\tau=l/v_F$, where l is the mean-free path of an electron with velocity v_F at the Fermi surface. For $\omega_0 \ll \omega_p$ ($\omega_s=\omega_p/\sqrt{2}$ is the surface plasmon frequency) we obtain

$$\boxed{\Gamma=\frac{2\mu^2}{d^3}\,\frac{\varepsilon_F}{\omega_p}\,\frac{1}{k_F l}\,\frac{\omega_0}{\omega_p},} \tag{3.29}$$

where it is assumed that $\mu_{\parallel}=0$. The formula (3.29) describes damping not only of the vibrational but also the electronic excitations of the molecule. According to (3.29) $\Gamma\sim d^{3}$; this prediction was checked experimentally.[37] The described bulk contribution to Γ corresponds to excitation of an electron-hole pair in the bulk of the metal, and in addition the excess momentum $\Delta k=k_f-k_i\sim k_F(\omega_0/2\varepsilon_F)$ is absorbed when electrons are scattered by phonons, impurities, or the crystalline potential (interband transitions) of the metal.

There also exists a purely surface contribution to Γ. First of all, the excess momentum can be adsorbed when an electron is scattered by the surface (S_1 process). Second, when the distance between the oscillator and the surface is small

$$d<\frac{2\varepsilon_F}{k_F\omega_0}$$

direct excitation of electron-hole pairs (Landau damping) is possible, since the field of the oscillator contains components with wave vectors right up to $1/d$ (S_2 process).

$$\Gamma_{S_1}=\frac{3[(\mu_{\parallel}^2/2)+\mu_{\perp}^2]}{2d^3}\,\frac{\omega_0}{\omega_p}\,\frac{1}{k_F d}, \tag{3.30}$$

$$\Gamma_{S_2}=\frac{9[(\mu_{\parallel}^2/2)+\mu_{\perp}^2]}{2d^3}\,\frac{\varepsilon_F\omega_0}{\omega_p^2}\,\frac{1}{k_F d}, \tag{3.31}$$

$$\Gamma\sim m_A^{-1}$$

the temparature dependence is weak

Electron-hole pair mechanism

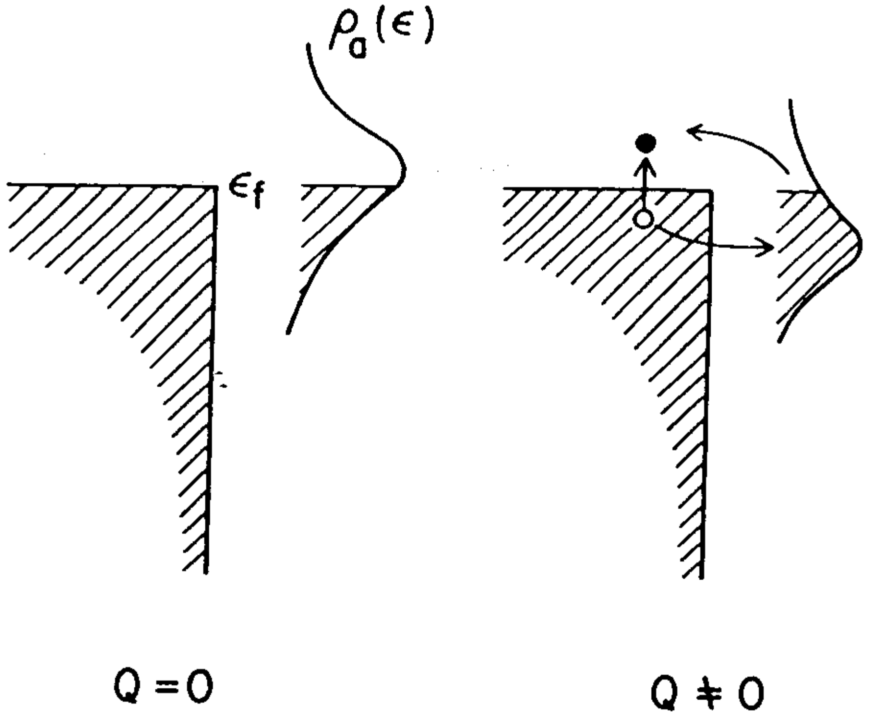


Fig. 5.8 Model of the non-adiabatic process of the EHP excitation due to the periodic filling and emptying of the adsorbate induced resonance state during molecular vibration.

$$\boxed{H = \sum_{\sigma} \varepsilon_a(Q)\, n_{a\sigma} + \sum_{k\sigma} \varepsilon_k n_{k\sigma} + \sum_{k\sigma} (V_{ak}(Q)\, c^{+}_{k\sigma} c_{a\sigma} + \text{h.c.}) + U n_{a\sigma} n_{a-\sigma} + \omega_0 b^{+} b,} \tag{3.37}$$

where $n_{k\sigma} = c^{+}_{k\sigma} c_{k\sigma}$, $n_{a\sigma} = c^{+}_{a\sigma} c_{a\sigma}$, and $c^{+}_{k\sigma}$ and $c^{+}_{a\sigma}$ are operators creating an electron in the states of the metal $|k\rangle$ and adatom $|a\rangle$ with energies ε_a and ε_k, V_{ak} is the hybridization matrix element, U is the coulomb repulsion energy between electrons with opposite spins σ on the adatom, $Q = (1/2m\omega_0)^{1/2}(b^{+} + b)$, and b^{+} is the phonon creation operator for local vibration of an adatom. In the presence of vibrations the position of the electronic level of the adatom ε_a and its width

$$\Delta = \pi \sum_k |V_{ak}|^2 \delta(\varepsilon - \varepsilon_k),$$

change, and this in its turn leads to oscillations of the charge of the adatom. The nonadiabatic nature of the charge oscillations leads to damping of the oscillations. Expanding $\varepsilon_a(Q)$ and $V_{ak}(Q)$ up to terms linear in Q and applying the linear-response theory in the quasiadiabatic limit $\boxed{(\Delta > \omega_0)}$ gives the following formula for the width of a vibrational level[17]

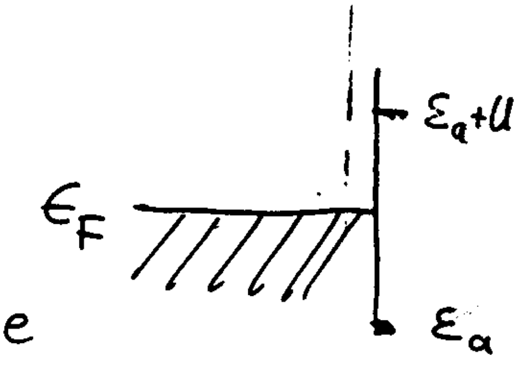
$$\boxed{\Gamma = \frac{4}{\pi m} \left\{ \underbrace{\sin^2 \delta(\varepsilon_F) \left[\frac{\langle |V'_{ak}|^2 \rangle_{\varepsilon_F}}{\langle |V_{ak}|^2 \rangle_{\varepsilon_F}} - \left(\frac{\Delta'}{2\Delta} \right)^2 \right]}_{\Gamma_1} + \underbrace{\frac{1}{2} (\delta'_{\varepsilon}(\varepsilon_F))^2}_{\Gamma_2} \right\},} \tag{3.38}$$

where $\langle \ldots \rangle$ indicates averaging over a surface with constant energy with $\varepsilon = \varepsilon_F$ and $\delta(\varepsilon_F)$ is the phase shift which, even for the case $U \neq 0$, is given by the expression

$$\delta(\varepsilon) = \text{arctg} \frac{\Delta(\varepsilon)}{\varepsilon_a - \varepsilon - \Lambda(\varepsilon) - \Sigma(\varepsilon)}$$

where

$$\Lambda(\varepsilon) = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\Delta(\varepsilon')}{\varepsilon - \varepsilon'} d\varepsilon'.$$



Temperature dependence

$(U = 0)$ $\quad \Gamma(T) = \Gamma(0)\left[1 + O\left(\left(\frac{T}{\Delta}\right)^2\right)\right]$

Kondo regime $(U \gg \Delta,\ |\varepsilon_a - \epsilon_F| \sim |\epsilon_a + U - \epsilon_F|)$

$$\boxed{\Gamma \sim m_A^{-1}}$$

$$\Gamma = \Gamma_1 + \Gamma_2$$

for vibration normal to the surface

$$\Gamma_\perp \simeq \underset{\uparrow}{\Gamma_2} = \frac{2}{\pi m_a}\left(\delta'(\epsilon_F)\right)^2$$

mechanism of charge transfer

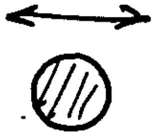
for vibration parallel to the surfac

$$\epsilon_a' = \Delta' = 0$$

$$\Gamma_\parallel = \underset{\uparrow}{\Gamma_1} = \frac{4}{\pi m_a}\sin^2\delta(\epsilon_F)\,\frac{\langle |V'_{ak}|^2\rangle_{\epsilon_F}}{\langle |V_{ak}|^2\rangle_{\epsilon_F}}$$

potential scattering mechanism

even symmetry



odd symmetr

<u>Selection rule</u>: The product of the adatom and substrate atom orbitals must to have the same symmetry with respect to a mirror plane of the surface as the vibrational mode of the adatom for the coupling between them to be nonzero.

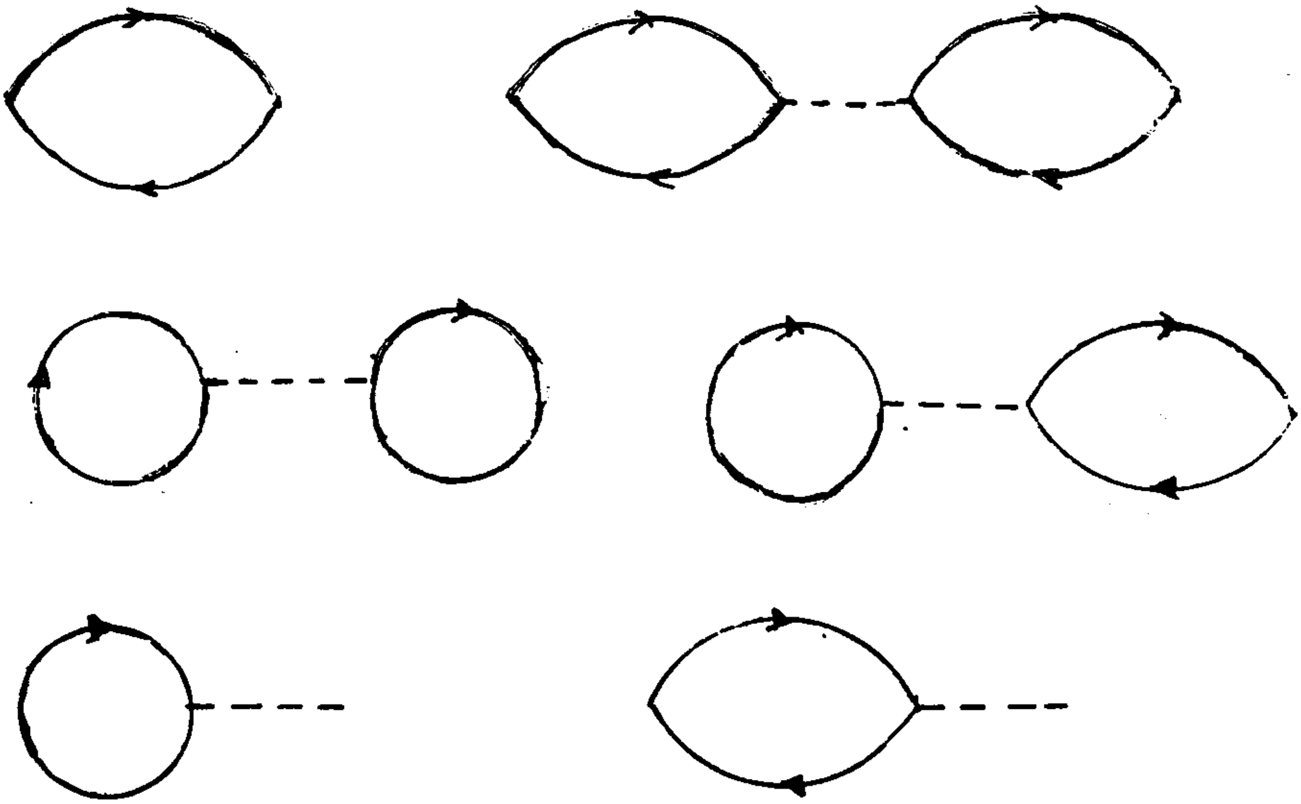
Asymmetric lineshape due to electron-hole decay mechanism

Vibration normal to the surface

Polarizability

$$\alpha(\omega) = \langle\langle \hat{p}, \hat{p} \rangle\rangle_\omega = \alpha_{e-e} + \alpha_{e-i} + \alpha_{i-e} + \alpha_{i-i}$$

$$\hat{p} = -ed\,\hat{n}_a + (1-\hat{n}_a)\,e Q_0 (b^+ + b)$$



$$\alpha(\omega) = \Pi(\omega) + D(\omega)$$

$$D(\omega) = p^2 \frac{2\omega_0}{\omega^2 - \omega_0^2 + i\omega\gamma}$$ Langreth, 198

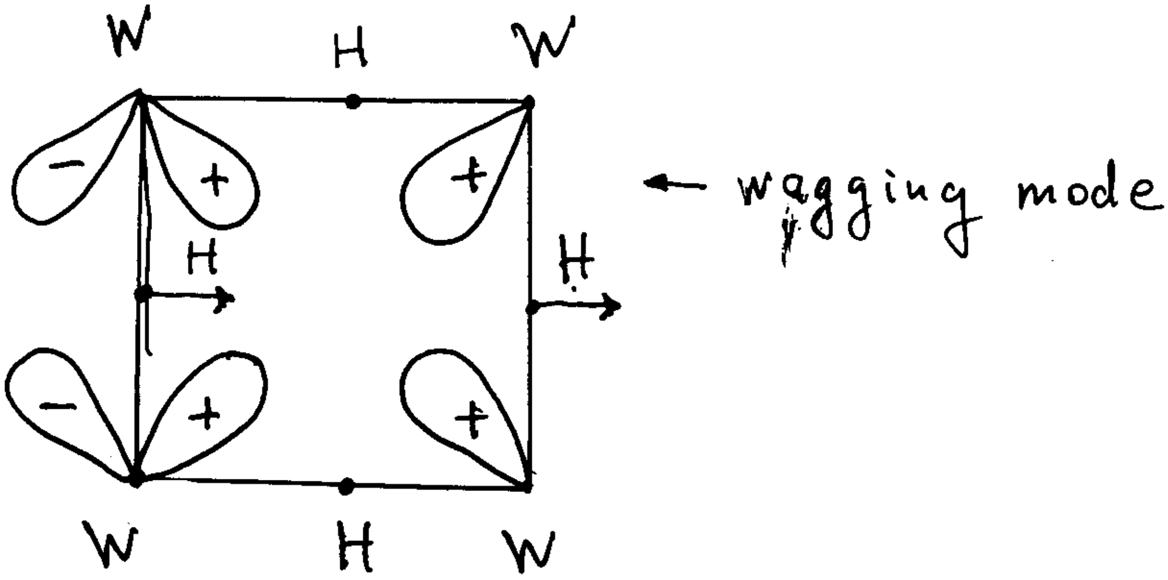
$$p = p_1 + i p_2$$

Vibrational lineshape

Asymmetric lineshape

Vibration parallel to the surface.

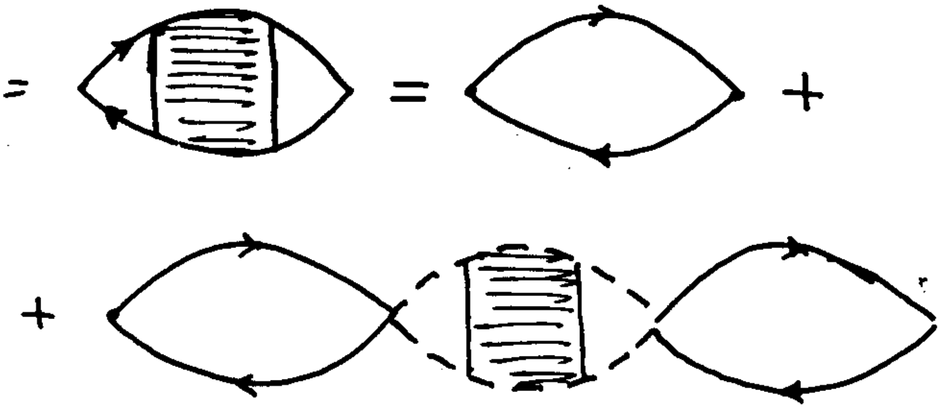
$$L(\omega) = \frac{2\omega_0 \mu_1^2}{\omega\gamma} \frac{\left[1 - \left(\frac{\omega^2-\omega_0^2}{\omega\gamma}\right)\omega\tau\right]^2}{1 + \left(\frac{\omega^2-\omega_0^2}{\omega\gamma}\right)^2}$$



$$H_{el\text{-}ph} = \frac{\delta\epsilon_2}{2}(b^+ + b)^2 \hat{n}_a + q_a \sum_k (V_{ak} c_a^+ c_k + h.c.)$$

$$H_I = \mu_0 \hat{n}_a (E_0 e^{i\omega t} + E_0^* e^{-i\omega t})$$

$L(\omega) =$

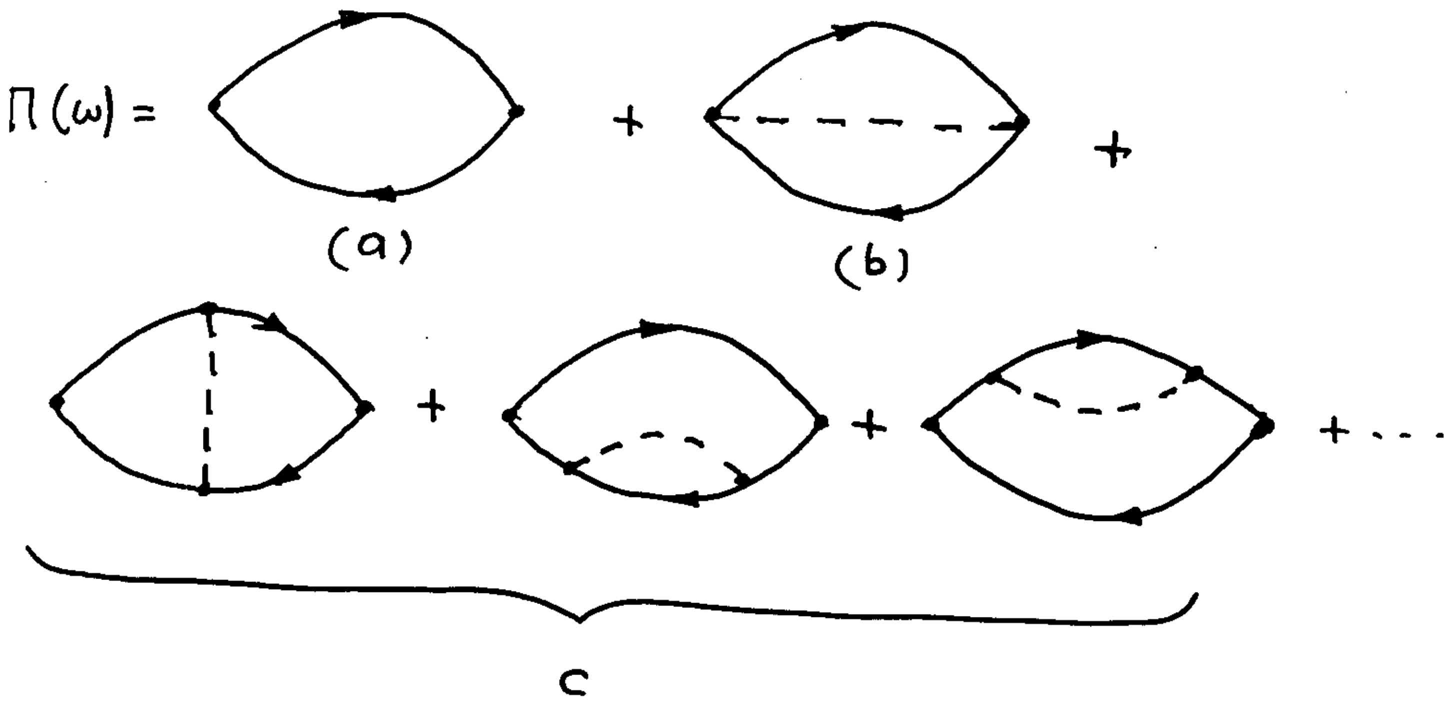


resonance at $\boxed{\omega = 2\omega_0}$

$$\ddot{q} + (\omega_0^2 + a\cos\omega t)\, q + \frac{\dot{q}}{T} = 0$$

Temperature dependence of linewidth

noninteracting electron ($U=0$)



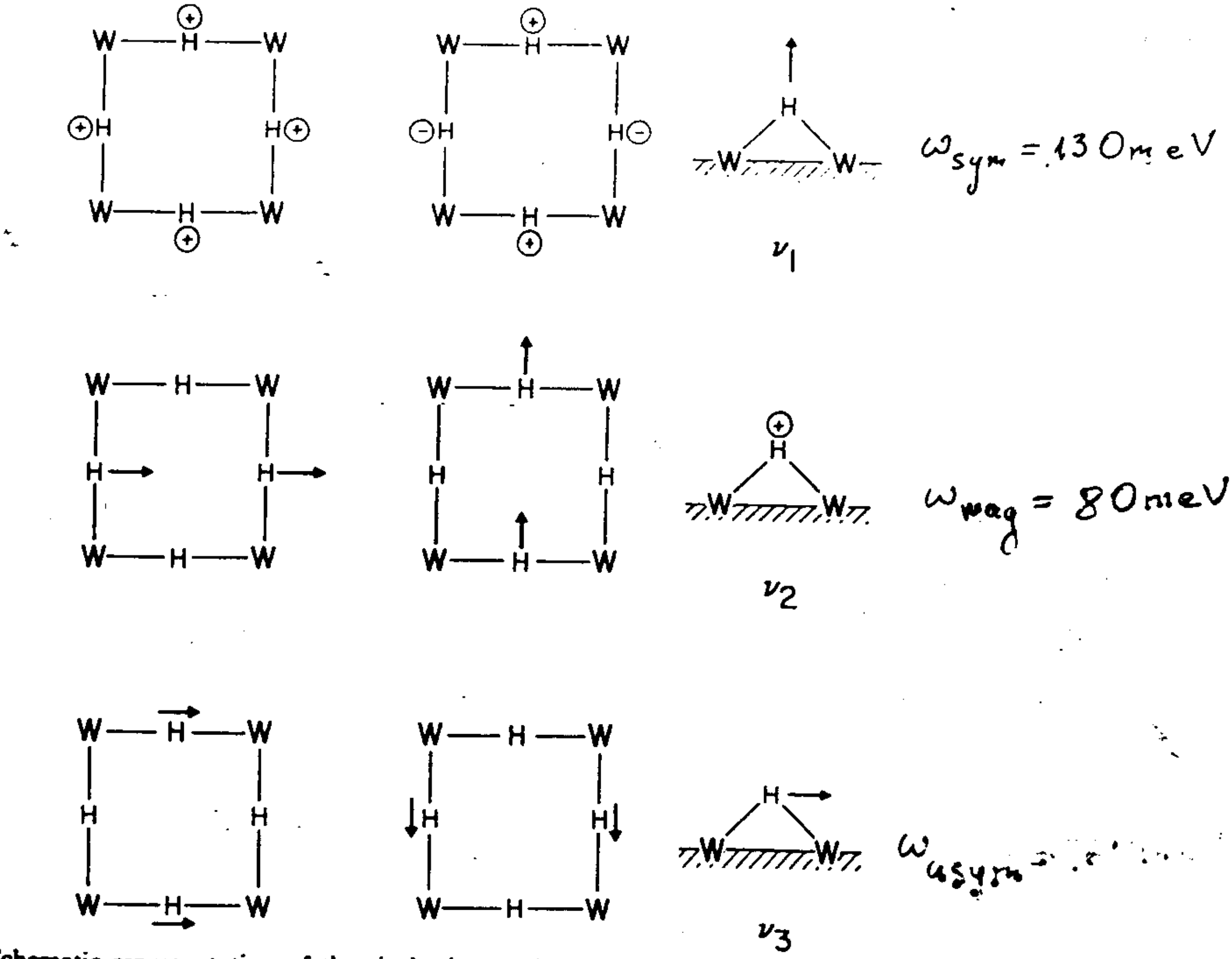
$$\Gamma_a = \Gamma_a(0) + \frac{\pi^2}{6}\frac{\partial^2 \Gamma_a}{\partial \epsilon^2}\bigg|_{\epsilon=0} T^2 = \Gamma_a(0)\left[1 + O\left(\left(\frac{T}{\Delta}\right)^2\right)\right]$$

$$\Gamma_b = 2\pi\left(\rho_a(0)\delta\epsilon_2\right)^2 T \sim \Gamma_a(0) \sim \Gamma_a(0)\left(\frac{Q_0}{d}\right)^2\frac{T}{\omega_0} \ll \Gamma_a$$

$$\Gamma_c = 8\pi(\delta\epsilon_1)^4 (g_a(0))^2 \rho_a^2(0)\, T \sim$$

$$\sim \Gamma_a(0)\left[4\pi^2\left(\frac{\delta\epsilon_1}{\Delta}\right)^2\frac{T}{\omega_0}\right] \sim (10^{-1} - 10^{-3})\,\Gamma_a(0)$$

The temperature dependence can be strong if the adatom is in a Kondo regime (U is large the level of the adatom ara arranged symmetrically with respect to the Fermi level and $T \sim T$

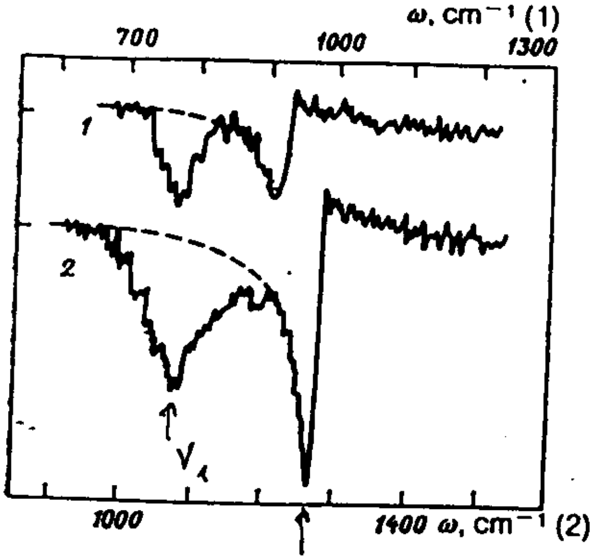


$\omega_{sym} = 130$ meV

$\omega_{wag} = 80$ meV

$\omega_{asym} =$ [illegible]

Fig. 50. Schematic representation of the six lattice modes associated with H in bridge position. Because there are 2 H per unit cell, there are two modes associated with each H displacement. These modes are degenerate for the ν_2 and ν_3 vibrations. For the ν_1 vibration, only the in-phase mode (top left) is infrared active. The out-of-phase (or optic) mode may have been observed by EELS in impact scattering [387] (from ref. [327]).



157.5 meV (1250 cm⁻¹)

FIG. 6. The vibrational spectra of D (1) and H (2) atoms adsorbed on W(100). The solid lines show the experimental data of Ref. 65 and the broken lines are theoretical curves from Refs. 65 and 66.

TABLE III. Damping parameters for vibrations of H and D on W (100).[65]

Atom	ω, cm⁻¹	γ, cm⁻¹	ωτ
H	1270	26	0.44
D	915	22	0.46

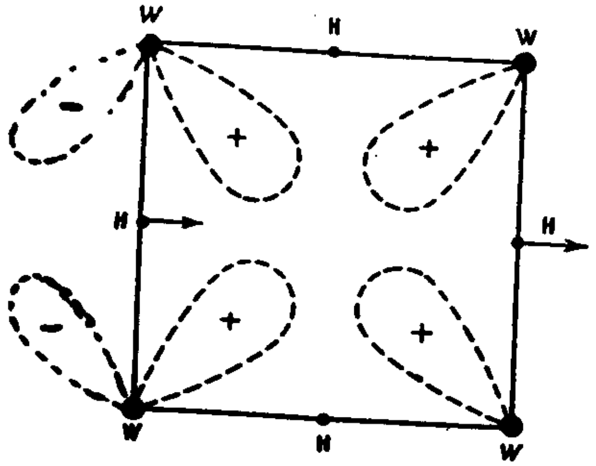


FIG. 7. A schematic diagram of the surface electronic states (broken lines) with which an H atom interacts under conditions of wagging vibrations. These states have d_{xy} symmetry (the z axis is perpendicular to the surface) and do not participate in the formation of a bond between hydrogen and tungsten.

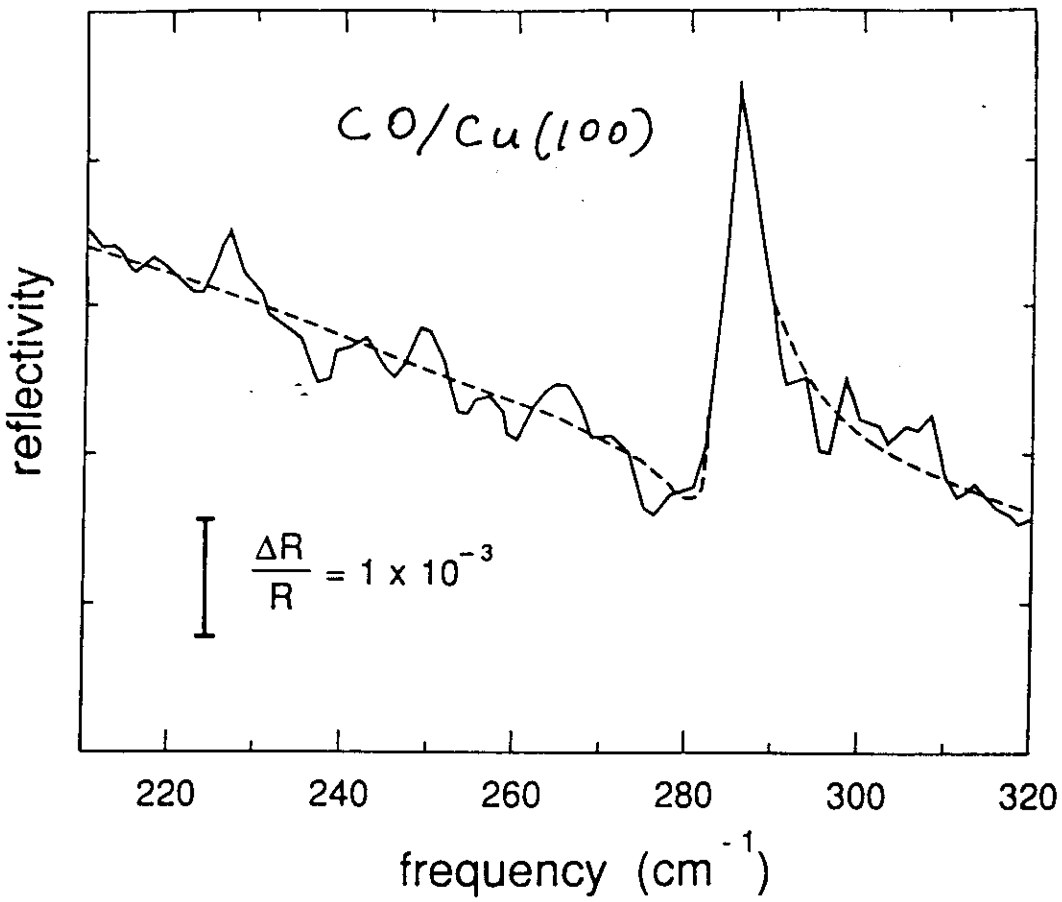
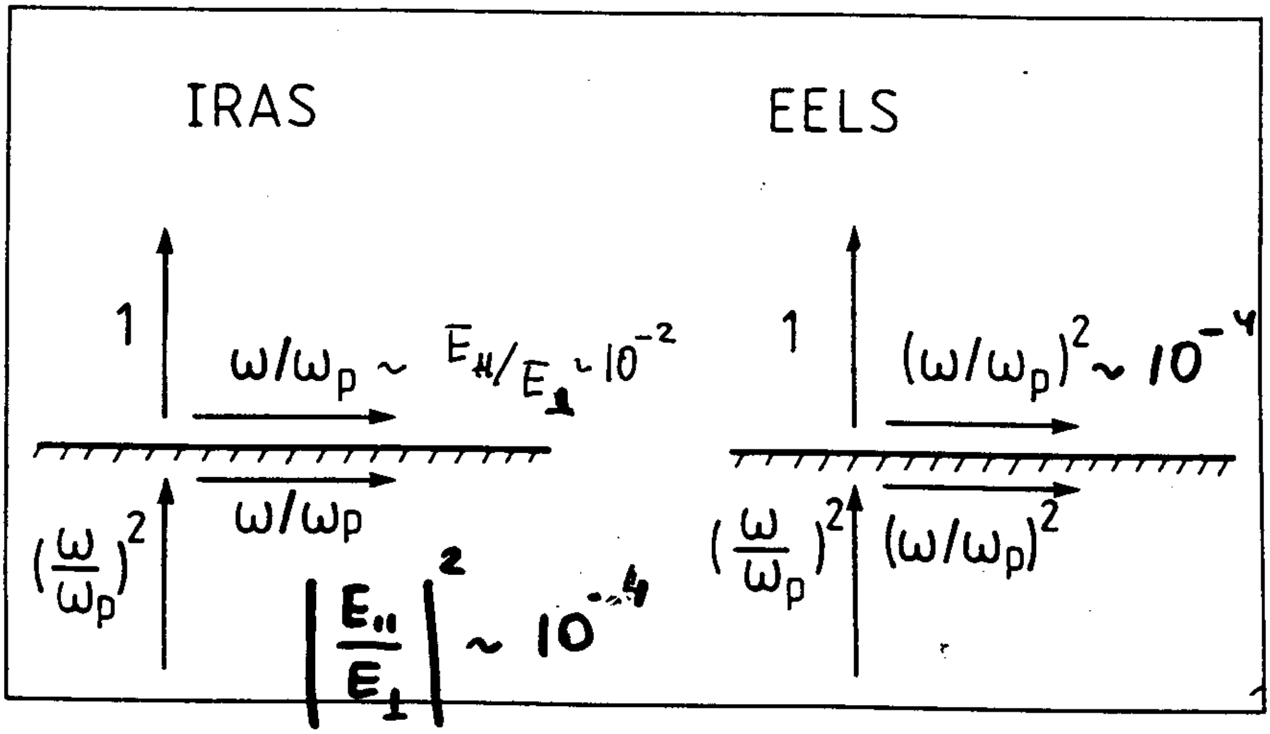

CO/Cu(100)
reflectivity
ΔR/R = 1 x 10^-3
220
240
260
280
300
320
frequency (cm^-1)

Fig. 1


IRAS
EELS
1
ω/ωp ~ E∥/E⊥ ~ 10^-2
ω/ωp
(ω/ωp)^2
|E∥/E⊥|^2 ~ 10^-4
1
(ω/ωp)^2 ~ 10^-4
(ω/ωp)^2
(ω/ωp)^2

~~12~~

Fig. 2

Persson, Volokitin
Chem. Phys. Lett. 1991. 185 (1991) 292

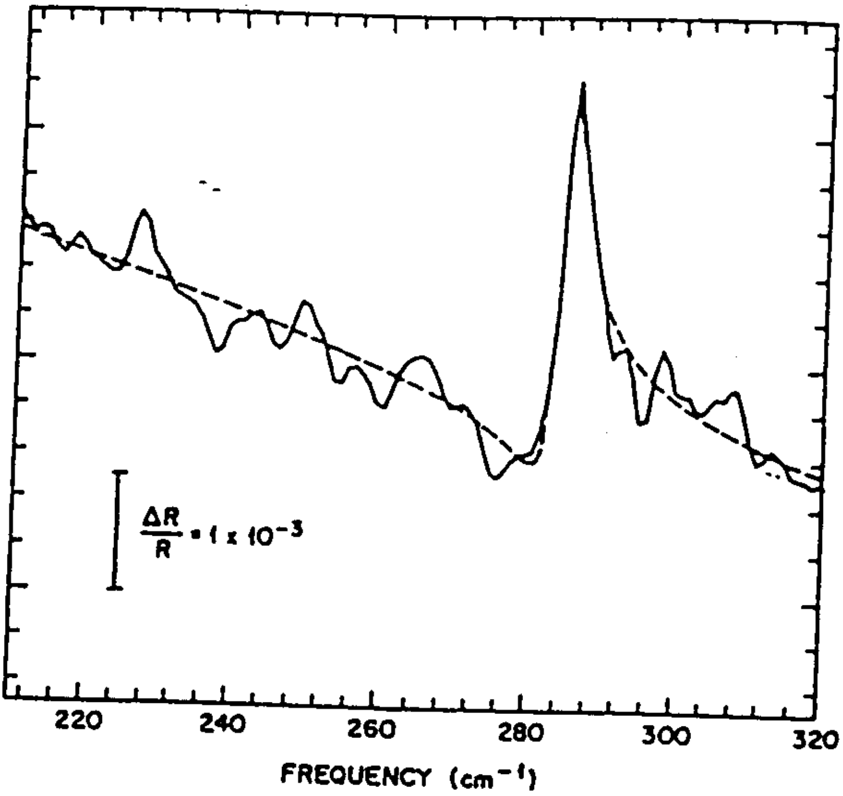
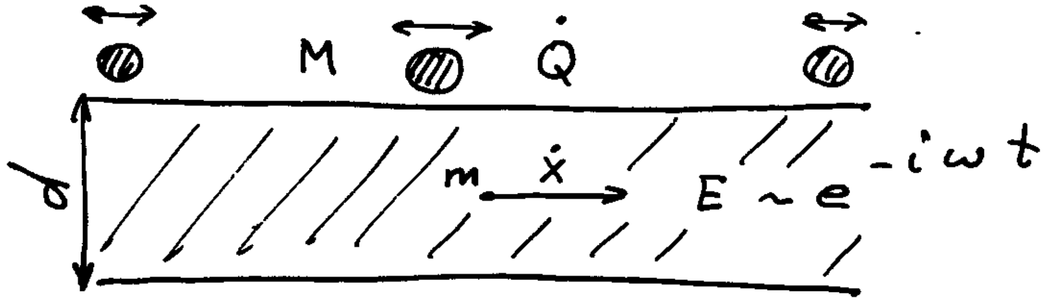


Fig. 1



$$\frac{\omega}{\omega_p} \sim \frac{v_F}{c}$$

$$\ddot{Q} + \Omega^2 Q + \frac{1}{\tau}(\dot{Q} - \dot{x}) = 0$$

$$\ddot{x} + \frac{1}{\tau_b}\dot{x} + \frac{M}{m}\frac{n_a}{n_e d \tau}(\dot{x} - \dot{Q}) = E_0 e^{-i\omega t}$$

$$\frac{\Delta R}{R} = -\frac{4 M n_a}{m n_e c \tau} \frac{(\Omega^2 - \omega^2)^2}{(\Omega^2 - \omega^2)^2 + (\omega/\tau)^2}$$

$$\boxed{\begin{matrix} \omega \gg \frac{1}{\tau_b} \\ \frac{\omega}{\omega_p} \gg \frac{v_F}{c} \end{matrix}}$$

Exchange model for phase relaxation

$$H = H_a + H_b + H_s + H_{ab} + H_{bs}$$

$$H_a = \omega_a a^+ a$$

$$H_b = \omega_b b^+ b$$

$$H_s = \sum_k \omega_k b_k^+ b$$

$$H_{ab} = \lambda a^+ a b^+ b$$

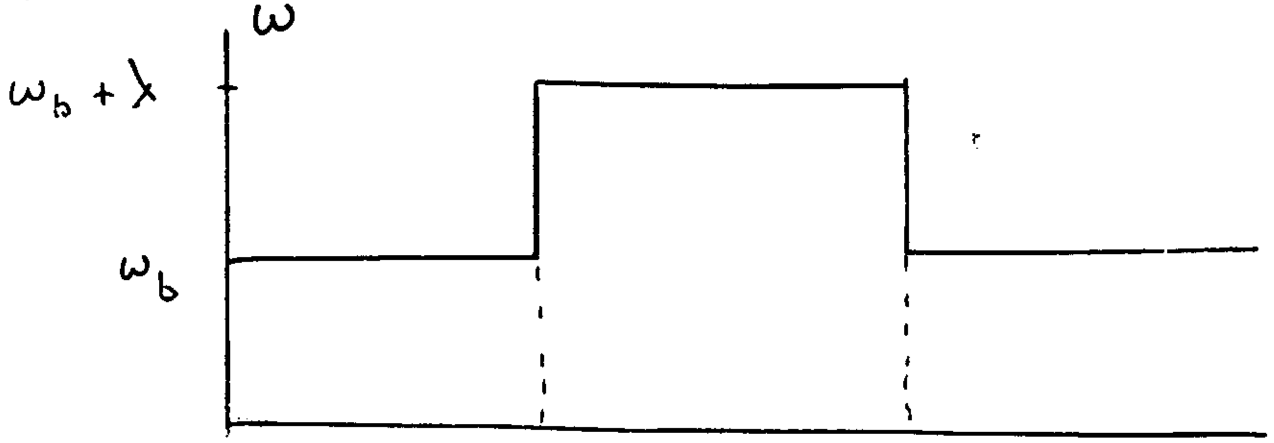
$$H_{bs} = \sum_k V_k b^+ b_k + \text{h.c.}$$

The exact solution for the lineshape

$$I(\omega) = \operatorname{Re} \int_0^\infty e^{i(\omega - \omega_a)t} s(t)\, dt$$

$$s(t) = \left\langle \hat{T} \exp\left[-i\lambda \int_0^t b^+(\tau) b(\tau)\right] \right\rangle$$

The solution of the problem is reduced to the finding of the response of the substrat phonons to the abrupt change of frequency ω_b (from ω_b to $\omega_b + \lambda$)



$$S(t) = e^{c(t)}$$

$$\frac{dc}{d\lambda} = \int_0^t G(\tau-0, \tau, t)\, d\tau$$

$$G(\tau, \tau', t) = -i \frac{\langle \hat{T}\, b(\tau)\, b^+(\tau')\, \hat{S}(t) \rangle}{\langle \hat{S}(t) \rangle}$$

$$G(\tau, \tau', t) = G_0(\tau-\tau') + \lambda \int_0^t G_0(\tau-\tau'')\, G(\tau'', \tau', t)\, d\tau''$$

In the quasimode approximation

$$G_0(\tau) = -i\, e^{-i\omega_b \tau - \Gamma_b |\tau|} \left[(1+n_b)\, \theta(\tau) + n_b\, \theta(-\tau) \right]$$

In this case the integral equation can be converted into the following differential equation

$$\frac{d^2 G}{d\tau^2} + i\lambda(\tau) \frac{dG}{d\tau} - \left[\Gamma_b^2 + i\lambda(\tau)\, \Gamma_b\, (2n_b+1) \right] G =$$

$$= -i \frac{d}{d\tau} \delta(\tau-\tau') + i\Gamma_b (2n_b+1)\, \delta(\tau-\tau') - i\lambda \left[G(0,\tau',t) \right.$$

$$\left. \times\, \delta(\tau) - G(t, \tau', \tau)\, \delta(\tau-t) \right], \qquad \lambda(\tau) = \lambda\left[\theta(\tau) - \theta(\tau-\right.$$

The lineshape is determined by

$$L(\omega) = -\operatorname{Im} (1-\xi) \frac{1-\xi\mu^2}{(1-\xi\mu)^2} \sum_{n=0}^{\infty} \frac{R^n}{\omega - \omega_a - \Delta\omega_n + i\Gamma_n}$$

Vibrational spectroscopy of adsorbates

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Present-day understanding of the nature of formation of vibrational spectra of adsorbates is examined. Particular attention is paid to the theoretical side of the problem. A comparison is made of the relative roles of T_1 (dissipative damping) and T_2 (pure dephasing) processes, and also of electron-hole pairs, phonons and photons in T_1 processes. The problem is discussed of separating out the mechanism dominating the determination of line shape. It is noted that inhomogeneous broadening which undoubtedly plays an important role in many cases has received little theoretical attention. An analysis is given of recent experimental data on the basis of modern theoretical concepts.

1. INTRODUCTION

Experimental methods for studying the vibrational spectra of adsorbates are an important part of surface physics. These methods include: inelastic scattering of neutrons and electrons, inelastic scattering of molecular beams, reflective IR spectroscopy, spectroscopy of surface polaritons, surface-enhanced Raman scattering, and time-resolved spectroscopy employing ultrashort pulses. The experimental methods of vibrational spectroscopy (VS) of adsorbates are described in detail in the collective monograph of Ref. 1. Vibrational spectroscopy has traditionally been employed for identifying the types of bonds in molecules. Since the characteristic frequencies of the bonds depend on the situation of the adsorbed molecule, in particular, to which of the atoms of the substrate this molecule is bound, there open up ways for analyzing the states, positions, and orientations of the molecules on the surface. In the process the spectral distribution of the intensity makes it possible to form estimates of the concentrations of particular adsorbed molecules. For example, when the H_2O molecule is adsorbed on the Si(100)—(2×1) surface frequencies characterizing the Si—H and O—H bonds are observed; this indicates that the H_2O molecule dissociates on adsorption.[2] The number of vibrational modes indicates the location at which the molecule is adsorbed. For example, for the system H/W(100) with coverage $\theta = 2$ there are three different modes,[3] which indicates unequivocally that the adsorption is of the B type, when the H atom lies between the two surface atoms of the substrate. On the other hand, for the system H/Ru(100) there are two different vibrational modes, indicating adsorption of the *c* type (centered).[4] The dependence of the vibrational frequency on the wave vector gives information about the force constants of the interaction between the adsorbed molecules. A shift of the frequency relative to its value in the gas phase indicates that the chemical bonds change as a result of chemisorption on the surface. Numerous examples illustrating how information about properties of adsorbates is obtained from frequency measurements are presented in Ref. 1.

A great deal of attention is now being devoted to the analysis of the shape of spectral lines. This is because the line shape contains important information about the lifetime of vibrations, the mechanisms of energy transfer, the inhomogeneity of the locations of adsorption, the mechanisms of interaction between adatoms, and the process of dephasing of the vibrations. Information on the vibrational relaxation of adsorbates is, in its turn, useful for interpreting other dynamic surface processes, such as diffusion, adsorption, and desorption. A detailed understanding of the nature of vibrational spectra of adsorbates is of fundamental importance for many areas of the physics and chemistry of surfaces, in particular, for heterogeneous catalysis. Over the last ten years extensive information has been accumulated in the field of interpretation of the shape of spectral lines, and the purpose of this review is to describe this information. The existing review articles[5] do not give a complete idea about this rapidly developing field.

2. THE SHAPE OF A SPECTRAL LINE

In this section we derive and discuss an expression for the reflecting power of an adlayer. Let *p*-polarized light with frequency ω, field strength $E(t) = E\cdot\mathrm{Re}\exp(i\omega t)$, and intensity $I_0 = cE_0^2/8\pi$, be incident on a surface at an angle β to the normal to the surface (Fig. 1). For the lowest-order nonadiabatic response of the electrons of the metal the action of the *p*-polarized incident and reflected waves is described by the quasistatic field $E_\perp(t)$, which at large distances from the surface is perpendicular to the surface. To calculate the reflecting power of the adlayer it is necessary to know how the electrostatic field varies in the space near the surface. To lowest order in $q = \omega/c$ it can be assumed that

$$E_\perp(t) = 2E_0 \sin\beta\,\mathrm{Re}\exp(i\omega t).$$

This expression holds for angles $\beta < 85°$; for $\beta > 85°$ the interference of the incident and reflected waves must be taken into account.[6] The energy of interaction of the external field with the dipole moment of the adsorbate equals $H_{\mathrm{int}} = -\hat{\mu}E_\perp(t)$, where $\hat{\mu}$ is the dipole-moment operator. According to the linear-response theory the energy adsorbed by vibrations per unit time per unit surface area equals[7]

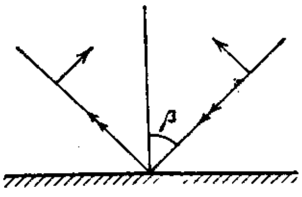

FIG. 1. Incidence of light on a surface.

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$$W = -\frac{1}{2}(2E_0 \sin\beta)^2 \omega N \,\mathrm{Im}\,\alpha(\omega), \qquad (2.1)$$

where N is the number of adsorbate molecules per unit area, while the generalized susceptibility $\alpha(\omega)$ is given by the expression

$$\alpha(\omega) = -i\int_0^\infty \exp(i\omega t)\langle[\hat\mu(t)\,\hat\mu(0)]\rangle\,\mathrm{d}t, \qquad (2.2)$$

where $\hat\mu(t)$ is the dipole-moment operator in the Heisenberg representation and $\langle\ldots\rangle$ indicates averaging over the grand canonical ensemble. Taking into account the fact that the intensity of the reflected light is reduced by an amount $W/\cos\beta$ we obtain for the reflecting power of the adlayer

$$\delta R = \frac{I_0 - I}{I_0} = -\frac{16\pi}{c}\frac{\sin^2\beta}{\cos\beta}N\omega\,\mathrm{Im}\,\alpha(\omega). \qquad (2.3)$$

The expression (2.3) holds in the limit of low coverage. For high coverage the value of N in the formula (2.3) must be set equal to unity, and $\alpha(\omega)$ must be interpreted as the generalized susceptibility of the entire system. Since $\mu = e^*Q$, where e^* is the dynamic charge of an admolecule and Q is the normal coordinate of the vibrations, $\alpha(\omega) = \mu^2 D^R(\omega)$, where μ is the dynamic dipole moment of the admolecule, which, generally speaking, can be a complex quantity,[8] i.e., $\mu = \mu_1 + i\mu_2$. The imaginary part μ_2 is related to the nonadiabaticity of the response of the electrons to the motion of the nuclei. $D^R(\omega)$ is the retarded phonon Green's function, which can be written in the form[9]

$$D^R\,\omega = 2\omega_0(\omega^2 - \omega_0^2 - 2\omega_0\Pi(\omega))^{-1}, \qquad (2.4)$$

where ω_0 is the frequency of the vibrations neglecting the interaction, which is included in the polarization operator $\Pi(\omega)$. The real part of the polarization operator determines the frequency shift while the imaginary part determines the FWHM:

$$\Delta\omega = \omega - \omega_0 = \mathrm{Re}\,\Pi(\omega_0), \qquad (2.5)$$

$$\Gamma = 2\,\mathrm{Im}\,\Pi(\omega_0). \qquad (2.6)$$

By virtue of the causality principle $\mathrm{Im}\Pi(\omega)$ and $\mathrm{Re}\Pi(\omega)$ are related by the Kramers–Kronig relation, so that any level-broadening mechanism will also lead to a frequency shift. If the linewidth is determined by energy transfer processes, then $\Gamma = 1/\tau$, where τ is the lifetime of the vibrations. Purely, phase relaxation processes could also be important. Elastic scattering of electrons and phonons by local vibrations of admolecules can lead to interruption of the phase of the vibrations, i.e., to dephasing of the vibrations. If at $t = 0$ all oscillators, which are assumed to be identical, have the same phase, then after a time t the phases of their vibrations will be different owing to random phase interruption. On time averaging the correlation function $\langle Q(t)Q(0)\rangle$ will be a decaying function of time. If this decay is exponential

$$\langle Q(t)\,Q(0)\rangle \sim \exp\left[-i(\omega_0 + \Delta\omega)t - \frac{\Gamma}{2}t\right], \qquad (2.7)$$

then the line shape

$$L(\omega) \sim \mathrm{Re}\int_0^\infty \exp(i\omega t)\langle Q(t)\,Q(0)\rangle\,\mathrm{d}t \qquad (2.8)$$

will be Lorentzian with width Γ. It is important to note that in the process the energy of the vibrations does not change, i.e., the amplitude of the vibrations remains constant. The line broadening associated with decay and dephasing of vibrations is often termed, respectively, longitudinal and transverse relaxation or T_1 and T_2 processes.

Line broadening also arises when the system is spatially disordered. For example, the surface of a crystal usually contains defects—steps, vacancies, impurity atoms, etc. The interaction between a defect and admolecules located near it brings about a change in the frequency of the vibrations of the admolecules, and averaging over an ensemble gives broadening of the vibrational line. The mechanism of line broadening owing to interaction between admolecules in the presence of structural defects in the adfilm is analogous. In an experiment it is important to know how to distinguish the

TABLE I. Vibrational frequency, line width, and dynamic charge for vibrations of adsorbed hydrogen (deuterium in parentheses).

Substrate	Mode	ω_0, MeV	Γ, MeV	e^*/e	Method	Reference
Ni (111)		88 (67)			EELS*)	[105]
		139 (90)			—	—
Ni (110), $\theta=1$		76		0.025	EELS	[106]
		117			—	—
		140			—	—
Ni (100)-c(2×2)	⊥	74 (52)			EELS	[107]
Ru (100), $\theta=1$	⊥	141 (101)	20—30		EELS	[108]
	∥	102 (74)	20—30		—	—
Pd (100)-c(2×2)	⊥	64			EELS	[109]
W (111)		160			EELS	[110]
W (110)		95			EELS	[110]
		157			—	—
W (100), $\theta=2$	⊥	133 (95)	11	0.053	IR	[65]
	∥	80			EELS	—
	∥	118			—	—
Pt (111)		68			EELS	[111]
		153			—	—
Si (111)-(7×7)	⊥	257		0.02	IR	[112]
Si (100)-(2×1)		258		0.04	IR	[2]

*) EELS—electron energy-loss spectroscopy

TABLE II. Frequency and line width of C═O vibrations accompanying adsorption of the CO molecule on the surface of some metals with low coverage (the results of measurements by the method of high-resolution IR spectroscopy (1 cm = 0.124 meV).

Metal	Coverage	ω_0, cm^{-1}	Γ, cm^{-1}	Reference
Ni (111)	0.16	1838	25	[113]
Ni (100)	<0.2	2030	50	[114]
Cu (111)	<0.2	2080	15	[115]
Cu (110)	0.1	2090	15	[116]
Cu (100)	0.17	2077	5	[117]
Ru (100)	0.05	1992	12	[118]
Pd (100)	0.14	1920	25	[119]
Pt (111)	0.32	2105	25	[120]
Pt (110)	0.1	2080	10	[121]
Pt (100)	<0.2	2082	7	[122]

contributions of different mechanisms to the measured width of a line. For this it is necessary to know the characteristic features of spectral lines associated with each specific mechanism of broadening. These features are studied in the following sections of this review.

The lifetime can be measured directly by the method of induced laser fluorescence, employing picosecond laser pulses.[10] The sensitivity of this method now permits studying adsorption only on colloidal silicon oxide, which has a large surface area. It has been found that for adsorption of the radicals OH, OD, BOH, and OCH_3 $\Gamma\tau$ equals 200–2000. For example, for the system OH/SiO_2 $\Gamma \approx 8$ cm^{-1} and $1/\tau \approx 2.6 \times 10^{-2}$ cm^{-1}.

Infrared radiation can excite only dipole-active modes, to which the transverse (perpendicular to the surface) vibrations refer. The longitudinal (parallel to the surface) vibrations usually are not dipole active; this is attributable to the fact that in the IR region of the spectrum the electric field is perpendicular to the surface, and the dipole moment of an admolecule is screened by the dipole moment of its mirror image. For this reason, for longitudinal vibrations the absorption peak at the fundamental frequency $\omega = \omega_0$ cannot be observed using IR spectroscopy. However the peak at the overtone frequency can be observed.[11]

The most extensive spectral data have been collected for vibrations of adsorbed H atoms and CO molecules. These data are summarized in Tables I and II.

3. ENERGY TRANSFER ACCOMPANYING VIBRATIONS OF ADSORBATES

In a vacuum the damping of the vibrations of a molecule occurs by means of a single mechanism—the radiation mechanism (with emission of a photon), for which, as is well known, $\tau^{-1} \approx \mu^2(\omega_0/c)^3$. On adsorption the lifetime of the vibrations decreases by many orders of magnitude; this indicates that the main mechanisms for the damping of the vibrations in this case are associated with excitation of quasiparticles of the substrate—phonons, electron-hole pairs, plasmons, etc. If the frequency of the vibrations of the molecules $\omega_0 > \omega_m$, where ω_m is the maximum frequency of the vibrational spectrum of the substrate, then damping of the vibrations of the admolecule owing to excitation of phonons is possible only owing to the anharmonicity of the vibrations. The electron-hole pairs are generated in the process of inelastic scattering of conduction electrons by the oscillating potential of a molecule. This potential can be separated into short- and long-range parts. The mechanism of damping associated with scattering by the short-range potential is simply called electron-hole damping. This mechanism can play the main role in chemisorption. Scattering of electrons by the long-range potential leads to the electromagnetic mechanism of damping, which plays an important role in physical adsorption. For metals the plasmon frequency is $\omega_p \gg \omega_0$, so that the plasmon mechanism of damping is inefficient for adsorption on metals. This mechanism can, however, be efficient for adsorption on semiconductors, for which it can happen that $\omega_p \approx \omega_0$.[12]

3.1. The phonon mechanism. In the case when the anharmonicity of the vibrations of the adsorbate is weak the diagram technique for temperature Green's functions can be employed to calculate the susceptibility $\alpha(\omega)$.[9] We shall write the total Hamiltonian of the anharmonic crystal in the form[11]

$$H = H_0 + H_{\text{int}}, \tag{3.1}$$

where H_0 is the Hamiltonian in the harmonic approximation and H_{int} denotes the anharmonic part of the potential. We shall illustrate the Green's functions technique using the simplest example—perpendicular surface vibrations of an adatom for A-type adsorption, when the interaction only with the nearest atom of the substrate is taken into account. In this case H_{int} depends only on the difference $u = Q_A - Q_S$, where Q_A and Q_S are the displacements of an adatom and an atom of the substrate from the position of equilibrium, so that H_{int} can be expanded in a power series in u:

$$H_{\text{int}} = \sum_{s=3}^{\infty} \lambda_s u^s. \tag{3.2}$$

We introduce the temperature Green's function[9]

$$D(\omega_n) = \int_0^\beta \exp(i\omega_n\tau) D(\tau)\, d\tau,$$
$$D(\tau) = -\langle T_\tau u(\tau) u(0)\rangle, \quad \omega_n = \frac{2\pi n}{\beta}, \tag{3.3}$$

where T_τ is the time-ordering operator and $\beta = 1/k_B T$. The Green's function satisfies Dyson's equation[9]

$$D = D_0 + D_0 \Pi D, \tag{3.4}$$

where $\Pi(\omega)$ is the polarization operator, determined by diagrams with no external lines, to calculate which the following rules are applicable:

1) to each phonon line there corresponds the function $D_0(\omega_n)$;

2) a factor λ_k is assigned to each vertex at which k phonon lines converge; and,

3) summation is performed over the free energy parameters $(\beta^{-1}\sum_{n=-\infty}^{\infty})$.

In the harmonic approximation Green's function $D_0(\omega_n)$ is given by the formula[12]

$$D_0(\omega_n)=\frac{1}{m_A}\,\frac{1-m_A\omega_n^2D_s(\omega_n)}{\omega_n^2+\omega_A^2-m_A\omega_A^2\omega_n^2D_s(\omega_n)}, \tag{3.5}$$

where $D_s(\omega_n)$ is the Green's function for a substrate atom

$$D_s(\omega_n)=-\int_0^{\beta}\exp(i\omega_n\tau)\langle T_\tau Q_s(\tau)Q_s(0)\rangle\,d\tau, \tag{3.6}$$

where ω_A is the vibrational frequency of an adatom on a rigid substrate. The retarded Green's function $D^R(\omega)$ can be found by analytical continuation of the function $D(\omega_n)$ from a discrete set of points $z_n=2\pi ni/\beta$ onto the real axis in the upper complex half-plane.[9] It follows from the formula (3.5) that taking into account the vibrations of substrate atoms leads to renormalization of the frequency of the vibrations, so that

$$\omega_0^2=\omega_A^2(1+m_A\omega_0^2\,\mathrm{Re}\,D_s^R(\omega_0)). \tag{3.7}$$

For $\omega_0<\omega_m$ the vibrations of the adatom are virtual and are characterized by the width

$$\Gamma=-\omega_0\omega_A^2m_A\,\mathrm{Im}\,D_s^R(\omega_0)=\frac{\pi}{2}\frac{m_A}{m_s}\omega_A^2\rho_s(\omega_0), \tag{3.8}$$

where $\rho_s(\omega)$ is the surface density of phonon states. The diagram technique is convenient in that it permits writing out any term in the perturbation theory. It was employed in Refs. 13 and 14 to describe the vibrations of adsorbates. At high temperatures, however, it becomes too cumbersome, since many terms of the perturbation series must be taken into account. For this reason, a different approach,[15,18] which permits taking into account in a compact manner the most important terms in the perturbation series to all orders, is presented below.

We shall write the Hamiltonian of the system in the form

$$H=H_l+H_p+H_{\mathrm{int}}, \tag{3.9}$$

$$H_l=\sum_\lambda\omega_\lambda b_\lambda^+b_\lambda, \tag{3.10}$$

$$H_p=(P^2/2m)+\langle V(Q,Q_A)\rangle, \tag{3.11}$$

$$H_{\mathrm{int}}=V(Q,Q_A)-\langle V(Q,Q_A)\rangle, \tag{3.12}$$

where H_l is the Hamiltonian of the lattice, H_p is the Hamiltonian describing the motion of an adparticle in the averaged potential $\langle V(Q,Q_A)\rangle$, H_{int} is the interaction Hamiltonian, Q_A is the coordinate of an adatom, Q is the set of phonon coordinates of the crystal, and m is the reduced mass. Averaging over the phonon coordinates of the substrate is performed:

$$\langle V(Q,Q_A)\rangle=\mathrm{Sp}_l(\rho_lV(Q,Q_A)), \tag{3.13}$$

$$\rho_l=\exp(-\beta H_l)Z_l^{-1},\quad Z_l=\mathrm{Sp}[\exp(-\beta H_l)]. \tag{3.14}$$

In the case when the anharmonicity of the potential $\langle V(Q,Q_A)\rangle$ is weak the Hamiltonian H_p can be written in the harmonic approximation

$$H_p=\omega_0b^+b, \tag{3.15}$$

and only the terms that are linear in the vibrational coordinate of the adatom need be included in H_{int}:

$$H_{\mathrm{int}}=Q_AV'(Q). \tag{3.16}$$

In this case the linear-response theory[7] gives the following result for the polarization operator:

$$\Pi(\omega)=-i\int_0^{\infty}\exp(i\omega t)\langle[(H_{\mathrm{int}}(t))_{01}(H_{\mathrm{int}}(0))_{10}]\rangle\,dt,$$
$$(H_{\mathrm{int}})_{01}=\langle 0|H_{\mathrm{int}}|1\rangle,\quad H_{\mathrm{int}}(t)=\exp(iH_lt)H_{\mathrm{int}}\exp(-iH_lt), \tag{3.17}$$

where $|0\rangle$ and $|1\rangle$ denote the ground and first excited state for vibrations of an adatom. The width of the level is given by the formula

$$\Gamma=(1+n(\omega_0))^{-1}\int_{-\infty}^{+\infty}\exp(i\omega_0t)c(t)\,dt,$$
$$c(t)=\langle(H_{\mathrm{int}}(t))_{01}(H_{\mathrm{int}}(0))_{10}\rangle,\ n(\omega)=[\exp(\beta\omega_0)-1]^{-1}. \tag{3.18}$$

If the Morse potential is employed for $V(Q,Q_A)$ and the interaction with the nearest substrate atoms only is taken into account (in this case Q is the coordinate of the vibrations of a surface substrate atom in the direction normal to the surface), then the function $c(t)$ has the form[16]

$$\begin{aligned}c(t)=D^2\{&B^2[\exp(4\alpha^2\langle Q(t)Q(0)\rangle)-1]\\&+4A^2[\exp(\alpha^2\langle Q(t)Q(0)\rangle)-1]\\&-4AB[\exp(2\alpha^2\langle Q(t)Q(0)\rangle)-1]\},\end{aligned} \tag{3.19}$$

where D is the energy of adsorption, $\alpha^2=m\omega_0^2/2D$, $A=(1/2k)(2k-3)^{1/2}$, $B=A(2k-1)/k$, and $k=(2mD)^{1/2}\alpha^{-1}$. In the harmonic approximation the correlation function of the substrate $\langle Q(t)Q(0)\rangle$ is determined by the expression

$$\begin{aligned}\langle Q(t)Q(0)\rangle&=\\&=\frac{1}{2m_s}\int_0^{\omega_M}\frac{\rho_s(\omega)}{\omega}[(1+n(\omega))\exp(-i\omega t)\\&\qquad+n(\omega)\exp(i\omega t)]\,d\omega,\end{aligned} \tag{3.20}$$

where m_s is the mass of a substrate atom and $\rho_s(\omega)$ is the density of the phonon states for transverse vibrations of a surface substrate atom. Since the term $\langle Q(t)Q(0)\rangle$ stands in the exponent of the expression (3.19) the formula (3.18) for Γ takes into account all multiphonon processes to second order in H_{int}, which corresponds to summation of the most important diagrams to all orders. The one-, two-, and three-phonon contributions to the level width can be obtained by expanding the function $c(t)$ in a series in $\langle Q(t)Q(0)\rangle$. For $\omega_0\gg\omega_m$ the integral (3.18) can be approximately calculated by the saddle-point method.[18,19] For this the contour of integration over t must be shifted into the upper half of the complex plane, where there is an infinite number of saddle points. Taking into account only the saddle point closest to the real axis and lying on the imaginary axis for Debye's model gives[18]

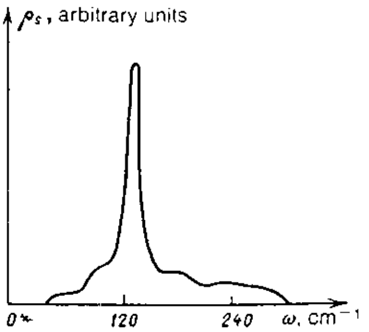

FIG. 2. The spectral density of the motion of atoms normal to the Ni(111) surface.

$$\Gamma = \frac{2\pi D^2}{(\omega_D\omega_0)^{1/2}} \exp\left[-\frac{\omega_0}{\omega_D}(y-1)\right], \qquad (3.21)$$

where $z = iy = i\omega_D\tau$ is the coordinate of the saddle point, which is determined from the equation

$$\frac{\exp y}{y} = \frac{1}{3}(1+n(\omega_D))^{-1}\frac{m_sD}{m\omega_0}\ . \qquad (3.22)$$

It follows from the formulas (3.21) and (3.22) that at high temperatures $\Gamma \sim T^n$, where $n = \omega_0/\omega_D$.[18,20] Calculations[18] using the formula (3.21) for transverse vibrations S ($\omega_0 = 360$ cm^{-1}) and 0 ($\omega_0 = 430$ cm^{-1}) on the Ni(100) surface at $T = 80$ K give $\Gamma_s = 34$ cm^{-1} and $\Gamma_0 = 30$ cm^{-1}, which agrees well with the experimental value of the linewidth obtained at the same temperature $\Gamma \approx 40$ cm^{-1}.[21]

Numerical calculation of the integrals (3.18) and (3.20) using a realistic function $\rho_s(\omega)$ (Fig. 2) for transverse vibrations of a CO molecule as a whole on the Ni(100) surface with A type adsorption was performed in Ref. 17 (Fig. 3). At room temperature ($T = 300$ K) the theoretical value of Γ (13.7 cm^{-1}) agrees well with the experimental value (15.3 cm^{-1}).[22] It is interesting that although decay into two phonons is possible ($\omega_0/\omega_D \approx 1.6$) the three-phonon process makes the main contribution to the linewidth. This is explained by the fact that the function $\rho_s(\omega)$ has a sharp peak at ≈ 135 cm^{-1}.

In the case of strong anharmonicity the shift in the positions of equilibrium of the atoms of the lattice accompanying the relaxation of the vibrations of the adsorbed particle must be taken into account in order to describe the vibration relaxation. The standard perturbation theory is not convenient in this case; generally speaking, many terms must be included in the perturbation series. To describe the "shift" adiabatic perturbation theory is traditionally employed.[23] The standard and adiabatic perturbation theories are sometimes contrated with one another on the grounds that they lead to different results.[23] As shown in Refs. 24 and 25, however, this difference is only apparent and is attributable to the fact that in the standard perturbation theory and the adiabatic perturbation theory different terms of the anharmonic potential coupling the oscillations are traditionally taken into account. Calculations[25] show that it is important to take into account the "shift" already for $n \geqslant 3$.

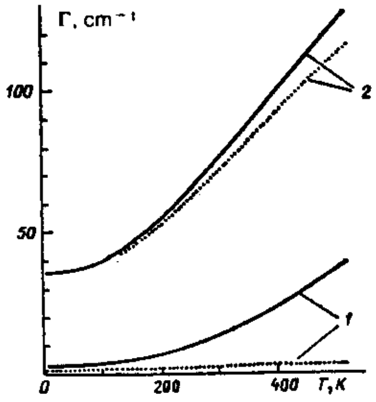

FIG. 3. The line width for CO=Ni vibrations for the system CO/Ni(111).[17] *1*—taking into account the spectral density $\rho_s(\omega)$ calculated in Ref. 26; *2*—Debye model. The dotted lines show the contribution of two-phonon processes.

Summarizing the results presented we note that the rate of decay of a local vibration into substrate phonons is determined primarily by the ratio $n = \omega_0/\omega_m$, as well as by the degree of anharmonicity of the vibrations. The phonon mechanism is characterized by a strong temperature dependence and a positive frequency shift $\Delta\omega > 0$. The contribution of multiphoton processes increases rapidly as the temperature increase $\Gamma \sim T^n$. There is also a strong isotopic effect. The phonon mechanism of decay is the main mechanism for $n \leqslant 3$. For high-frequency vibrations $n > 3$ the electron-hole mechanism studied below is more efficient.

3.2. The electromagnetic mechanism. If a molecule is physically adsorbed or is located quite far from the surface of the metal, the electric field from the oscillating dipole of the molecule penetrates into the bulk of the metal, and this generates electron-hole pairs. The Hamiltonian for the interaction of the vibrations of the molecule and the electrons of the metal has the form

$$H_{\text{int}} = Q_A \int g(\mathbf{r})\,\hat\rho(\mathbf{r})\,d^3\mathbf{r}, \qquad (3.21')$$

where Q_A is the normal coordinate of the vibrations, $Q_A g(\mathbf{r})$ is the change in the potential energy of the molecule accompanying a displacement of the normal coordinate from the position of the equilibrium by an amount Q_A, and $\hat\rho(\mathbf{r})$ is the electron density operator for the metal. In the linear-response approximation the polarization operator can be represented in the form

$$\Pi(\omega) = \int d^3\mathbf{r}' \int d^3\mathbf{r}\,\varphi(\mathbf{r})\,\chi(z, z', \mathbf{x}-\mathbf{x}', \omega)\,\varphi(\mathbf{r}'), \qquad (3.23)$$

where $\varphi(\mathbf{r})$ is the potential of a point dipole with the dipole moment

$$\mu = e^*Q_0 = e^*(2m\omega_0)^{-1/2}.$$

The charge-density response function for a semiinfinite metal [$\mathbf{r} = (\mathbf{x}, z)$; the metal is assumed to occupy the half-space $z < 0$] is given by the formula

$$\chi(z, z', \mathbf{x}-\mathbf{x}', \omega) = \sqrt{-i}\int_0^\infty \exp(i\omega t)\langle[\hat\rho(\mathbf{r}, t),\ \hat\rho(\mathbf{r}', 0)\rangle\,dt. \qquad (3.24)$$

Introducing the function

$$g(q_\parallel, \omega) = \frac{2\pi}{q_\parallel}\int dz \int dz' \exp[q_\parallel(z+z')]\,\chi(z, z', \mathbf{q}_\parallel, \omega), \qquad (3.25)$$

where

$$\chi(z, z', \mathbf{q}_{\parallel}, \omega) = \int \exp(i\mathbf{q}_{\parallel}\mathbf{x})\chi(z, z', \mathbf{x}, \omega)\, d^2\mathbf{x}, \qquad (3.26)$$

and carrying out the two-dimensional Fourier transform in the integrand in (3.23) gives[27,28]

$$\Pi(\omega) = \left(\frac{\mu_{\parallel}^2}{2} + \mu_{\perp}^2\right) \cdot \frac{1}{2}\int_0^{\infty} q_{\parallel}^2 \exp(-2q_{\parallel}d)\, g(q_{\parallel}, \omega)\, d q_{\parallel}, \qquad (3.27)$$

where d is the distance between the point dipole and the surface of the metal; $\mu_{\parallel}$ and $\mu_{\perp}$ are the components of the dipole moment parallel and perpendicular to the surface; $g(q_{\parallel},\omega)$ is the linear-response function employed for describing many processes at a surface, including the van-der-Waals force between an atom and the surface of a metal, the surface photoeffect, friction for motion of charged particles near the surface,[29] etc. As shown in Ref. 30 the function $g(q_{\parallel},\omega)$ can be determined experimentally with the help of inelastic scattering of slow electrons.

A large number of publications,[28,31-35] in which the electromagnetic mechanism of damping is analyzed differ by the form of the approximation employed for the function $g(q_{\parallel},\omega)$. If spatial dispersion is neglected, i.e., the metal is described by a local permittivity, equal to the bulk value of $\varepsilon(\omega)$ for $z<0$ and unity for $z>0$, then the response function can be expressed in terms of the permittivity[36]

$$g(q_{\parallel}, \omega) = (\varepsilon(\omega) - 1)(\varepsilon(\omega) + 1)^{-1}. \qquad (3.28)$$

In Drude's approximation $\varepsilon(\omega) = 1 - [\omega_p^2/\omega(\omega + i\tau)]$, where ω_p is the bulk plasma frequency, $\tau = l/v_F$, where l is the mean-free path of an electron with velocity v_F at the Fermi surface. For $\omega_0 \ll \omega_2$ ($\omega_s = \omega_p/\sqrt{2}$ is the surface plasmon frequency) we obtain

$$\Gamma = \frac{2\mu^2}{d^3}\frac{\varepsilon_F}{\omega_p}\frac{1}{k_F l}\frac{\omega_0}{\omega_p}, \qquad (3.29)$$

where it is assumed that $\mu_{\parallel} = 0$. The formula (3.29) describes damping not only of the vibrational but also the electronic excitations of the molecule. According to (3.29) $t \sim d^3$; this prediction was checked experimentally.[37] The described bulk contribution to Γ corresponds to excitation of an electron-hole pair in the bulk of the metal, and in addition the excess momentum $\Delta k = k_f - k_i \sim k_F(\omega_0/2\varepsilon_F)$ is absorbed when electrons are scattered by phonons, impurities, or the crystalline potential (interband transitions) of the metal.

There also exists a purely surface contribution to Γ. First of all, the excess momentum can be adsorbed when an electron is scattered by the surface (S_1 process). Second, when the distance between the oscillator and the surface is small

$$d < \frac{2\varepsilon_F}{k_F\omega_0}$$

direct excitation of electron-hole pairs (Landau damping) is possible, since the field of the oscillator contains components with wave vectors right up to $1/d$ (S_2 process). The calculation turns out to be quite complicated because of the need to take into account spatial dispersion,[31-35] and the results are sensitive to the model employed (the selected profile of the electron distribution). In particular, for the jellium model it was found[33] that

$$\Gamma_{S_1} = \frac{3[(\mu_{\parallel}^2/2) + \mu_{\perp}^2]}{2d^3}\frac{\omega_0}{\omega_p}\frac{1}{k_F d}, \qquad (3.30)$$

$$\Gamma_{S_2} = \frac{9[(\mu_{\parallel}^2/2) + \mu_{\perp}^2]}{2d^3}\frac{\varepsilon_F\omega_0}{\omega_p^2}\frac{1}{k_F d}, \qquad (3.31)$$

where ξ_F is a constant ($\simeq 1$). It follows from the expressions (3.30)–(3.31) that $\Gamma_s \sim d^{-4}$. Since for a metal substrate $l \sim 100$ Å in the infrared region the "surface" makes the main contribution to Γ. Calculations[28,32] show that when CO and N_2 molecules are adsorbed on the surface of the metals Cu and Pt the electromagnetic broadening of the spectral line is less than 10% of the experimentally observed value. The electromagnetic mechanism also leads to a small frequency shift. For vibrations of the C=O bond accompanying adsorption of CO on the Cu(100) surface $\Delta\omega_{el} = -2$ cm^{-1}.[35] The foregoing theory is, generally speaking, limited by processes which include small values of $q_{\parallel}$ (and thus large d, since $q_{\parallel} \lesssim 1/d$). The corrections arising from components with large $q_{\parallel}$ were evaluated in Ref. 38.

The electromagnetic mechanism can play an important role in adsorption on the surface of a semiconductor or semimetal, when the frequency ω_0 is close to one of the characteristic frequencies of the collective excitations of the substrate, in particular, the surface plasmon frequency ω_s (for the surface of a semiconductor $\omega_s = (4\pi e^2 n/(\varepsilon_0 + 1)m^*)^{1/2}$, where n is density of conduction electrons (holes) with effective mass m^* and ε_0 is the static permittivity). In this case[12]

$$\Gamma = \frac{\mu^2\omega_s\delta_s^{-1}}{8(\varepsilon_0 + 1)d^3}, \qquad (3.32)$$

where δ_s is the damping decrement of surface plasmons. If $\delta_s \lesssim \omega_s$, damping will occur primarily by the electromagnetic mechanism.

In concluding this section we note that for the electromagnetic damping mechanism there is an isotopic effect ($\Gamma \sim m_A^{-1}$, since $\mu^2 \sim m_A^{-1}$), but the temperature dependence turns out to be weak.

3.3. The electron-hole mechanism. In the process of chemisorption the interaction of vibrations of the adsorbate with the electrons of the metal is described by the well developed theory of electron-phonon interaction.[39] The expression for the polarization operator is determined, as before, by the formula (3.2), in which $\varphi(\mathbf{r})$ represents the change in the potential of the adsorbate when the normal coordinate of the vibrations Q is increased by an amount equal to the transition matrix element $Q_0 = (1/2m\omega_0)^{1/2}$, i.e.,

$$\varphi(\mathbf{r}) = \frac{\partial V(Q, \mathbf{r})}{\partial Q}Q_0,$$

where $V(Q,\mathbf{r})$ is the potential of the adsorbate. For practical calculations it is convenient to rewrite the formula (3.3) in the form

$$\Pi(\omega) = \int d^3r \int d^3r'\, \tilde{\varphi}(\mathbf{r})\, \tilde{\chi}(\mathbf{r}, \mathbf{r}')\, \tilde{\varphi}(\mathbf{r}'), \qquad (3.33)$$

where $\varphi(\mathbf{r})$ is the screened change in the potential and $\chi(\mathbf{r},\mathbf{r}')$ is the irreducible part of the charge-density response function, which determines the response of the electrons in the metal to the screened change in the potential (the irreducible part does not contain diagrams that can be divided into two parts separated by one coulomb line). In the random-phase approximation

$$\tilde{\chi}(\mathbf{r},\mathbf{r}')=2\sum_{k,k'}\frac{\psi_k(\mathbf{r})\,\psi^*_{k'}(\mathbf{r})\,\psi_{k'}(\mathbf{r}')\,\psi^*_k(\mathbf{r})}{\omega-\varepsilon_k-\varepsilon_{k'}+i\delta}$$

$$f(\varepsilon_k)\,(1-f(\varepsilon_{k'}))+(\omega\to-\omega), \qquad (3.34)$$

where $\tilde{\psi}_k(\mathbf{r})$ and ε_k are the single-electron wavefunctions and energies, $f(\varepsilon_k)$ is the Fermi distribution function, and the factor of 2 arises owing to summation over the electron spins. Substituting (3.34) into the formula (3.31) gives the following expression for the width of a level[40]

$$\Gamma=\frac{2\pi}{m}\sum_{k,k'}\left|\int d^3\mathbf{r}\,\psi_k(\mathbf{r})\frac{\partial V(Q,r)}{\partial Q}\,\psi_{k'}(\mathbf{r})\right|^2,\quad \varepsilon_k=\varepsilon_{k'}=\varepsilon_F. \qquad (3.35)$$

For a homogeneous medium the formula for Γ can be presented in the form[40,43]

$$\Gamma=\left(\frac{9}{4\pi}\right)^{1/3}\frac{3}{mr_s^2}\sum_{l=0}^{\infty}(l+1)\sin^2(\delta_{l+1}-\delta_l), \qquad (3.36)$$

where δ_l are the phase shifts for scattering of an electron with the Fermi energy by the potential of the adatom and r_s is the electron density parameter ($4\pi r_s^3/3=n$; n is the electron density). The expression (3.36) can be employed to make a rough estimate of Γ at the surface, if the local values of the phases are employed for δ_l.[41]

The formula (3.35) serves as a basis for numerical calculations of the rate of vibrational relaxation in the jellium model within the framework of the density functional method[40–42] (see, for example, Fig. 4). The width Γ has also been calculated by the method of linear combination of atomic orbitals (LCAO).[44]

In spite of the importance of calculations based on first principles the Anderson-Newns semiempirical model[14,17,45–48] plays a large role in elucidating the physical essence of the electron-hole mechanism of damping and establishing a correlation with the experimental data. The Anderson-Newns Hamiltonian has the form[49]

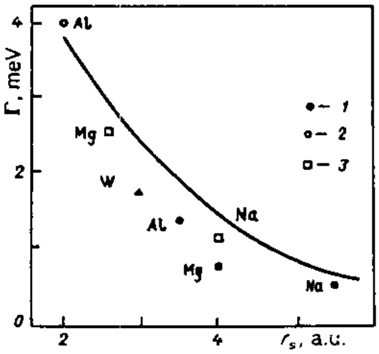

FIG. 4. The rate of relaxation of vibrations of a hydrogen atom normal to the surface as a result of the excitation of electron-hole pairs (calculation of Ref. 40 on the basis of the jellium model). The solid line shows the calculation for a uniform electron gas; the separate points correspond to different distances from the proton to the jellium boundary: 1) equilibrium distance; 2) $d=-2$ a.u.; 3) $d=-14$ a.u.; for tungsten the experimental value is given.

$$H=\sum_{\sigma}\varepsilon_a(Q)\,n_{a\sigma}+\sum_{k\sigma}\varepsilon_k n_{k\sigma}+\sum_{k\sigma}(V_{ak}(Q)\,c^+_{k\sigma}c_{a\sigma}+\text{h.c.})$$
$$+\,Un_{a\sigma}n_{a-\sigma}+\omega_0 b^+b, \qquad (3.37)$$

where $n_{k\sigma}=c^+_{k\sigma}c_{k\sigma}$, $n_{a\sigma}=c^+_{a\sigma}c_{a\sigma}$, and $c^+_{k\sigma}$ and $c^+_{a\sigma}$ are operators creating an electron in the states of the metal $|k\rangle$ and adatom $|a\rangle$ with energies ε_a and ε_k, V_{ak} is the hybridization matrix element, U is the coulomb repulsion energy between electrons with opposite spins σ on the adatom, $Q=(1/2m\omega_0)^{1/2}(b^++b)$, and b^+ is the phonon creation operator for local vibration of an adatom. In the presence of vibrations the position of the electronic level of the adatom ε_a and its width

$$\Delta=\pi\sum_k|V_{ak}|^2\,\delta(\varepsilon-\varepsilon_k),$$

change, and this in its turn leads to oscillations of the charge of the adatom. The nonadiabatic nature of the charge oscillations leads to damping of the oscillations. Expanding $\varepsilon_a(Q)$ and $V_{ak}(Q)$ up to terms linear in Q and applying the linear-response theory in the quasiadiabatic limit ($\Delta\gg\omega_0$) gives the following formula for the width of a vibrational level[17]

$$\Gamma=\frac{4}{\pi m}\left\{\sin^2\delta(\varepsilon_F)\left[\frac{\langle|V'_{ak}|^2\rangle_{\varepsilon_F}}{\langle|V_{ak}|^2\rangle_{\varepsilon_F}}-\left(\frac{\Delta'}{2\Delta}\right)^2\right]+\frac{1}{2}(\delta'_\perp(\varepsilon_F))^2\right\}, \qquad (3.38)$$

where ⟨...⟩ indicates averaging over a surface with constant energy with $\varepsilon=\varepsilon_F$ and $\delta(\varepsilon_F)$ is the phase shift which, even for the case $U\neq0$, is given by the expression

$$\delta(\varepsilon)=\operatorname{arctg}\frac{\Delta(\varepsilon)}{\varepsilon_a-\varepsilon-\Lambda(\varepsilon)},$$

where

$$\Lambda(\varepsilon)=\frac{1}{\pi}\int_{-\infty}^{\infty}\frac{\Delta(\varepsilon')}{\varepsilon-\varepsilon'}\,d\varepsilon'.$$

The derivation of the formula (3.38)[17] employed the relation[17,41] between the linewidth and the coefficient of friction

$$\Gamma=\eta \qquad (3.39)$$

for excitation of electron-hole pairs, which is valid for $\Delta\gg\omega_0$, as well as the coefficient of friction calculated in Ref. 50.

The fact that the formula (3.38) for Γ is identical for both $U=0$ and for $U\neq0$ is linked with the fact that the imaginary part of the self-energy part of the electronic Green's function of the adatom, associated with the Coulomb interaction U, vanishes at the Fermi energy.[51]

The formula (3.38) contains two substantially different terms. For transverse oscillations the first term turns out to be small; in particular, the first term vanishes identically if $V_{ak}(Q)=f(Q)V_{ak}$. For longitudinal vibrations, for which $\varepsilon'_a=\Delta'=0$, the second term vanishes. One can see that the first term is reminiscent of the well-known formula for the resistance of a metal.[52] Indeed, both formulas are equivalent, if the surface is smooth and scatters electrons specularly and the Fermi surface is spherical. The mechanism for damping of oscillations associated with the second term is termed the mechanism with charge transfer, while the mechanism associated with the first term is termed the potential-scattering mechanism.

The formula (3.38) shows that the mechanism with charge transfer and the potential-scattering mechanism are related with the interaction of the orbitals of the adatom with the orbitals of the substrate atoms, whose symmetry is different. In particular, if the adatom orbital has σ symmetry, then the mechanism with charge transfer is related to the interaction with the orbitals of the substrate atoms, which also have σ symmetry, while the potential-scattering mechanism is related to the orbitals having π-symmetry, which do not participate in the formation of a chemisorption bond.

For noninteracting electrons ($U = 0$) the temperature dependence of Γ has the form

$$\Gamma(T) = \Gamma(0)\,(1 + O(k_B T \Delta^{-1}))^2,$$

i.e., it is weak when $k_B T \ll \Delta$.[17] The temperature dependence, however, can be strong, if the adatom is in a Kondo regime (U is large, the levels of the adatom are arranged symmetrically with respect to the Fermi level, and $T \approx T_K$, where T_K is the Kondo temperature). Calculations[14,17,47] show that for chemisorption of hydrogen on the surface of transition metals $\Gamma_\perp \approx \Gamma_\parallel \approx 275$ meV.

For transverse vibrations the formulas for the level width and the frequency shift can be written in the form[17,45,46]

$$\Gamma = 2\pi\omega_0 (\delta n)^2, \tag{3.40}$$

$$\Delta\omega = -\lambda \delta n, \tag{3.41}$$

where $\lambda = (1/2m\omega_0)^{1/2}|\varepsilon_a'|$, δn is the charge of an admolecule accompanying a shift in its position of equilibrium by an amount $Q_0 = (1/2m\omega_0)^{1/2}$, and m is the reduced mass. We note that the electron-hole mechanism is characterized by a "red" shift of the vibrational frequency ($\Delta\omega < 0$). For vibrations of the C=O bond accompanying adsorption of CO on the Cu(100) surface, according to the experimental data $\delta n = 0.3$,[46] $|\varepsilon_a'| = 11$ eV/Å,[53] and $\omega_0 = 2084\ \text{cm}^{-1}$.[54] Using these values and taking into account the spin and orbital degeneracy of the $2\pi^*$ orbitals of the CO molecule we obtain $\Gamma = 3\ \text{cm}^{-1}$ (Ref. 46) and $\Delta\omega = -88\ \text{cm}^{-1}$ (Refs. 17 and 55). The theoretical value of Γ is in good agreement with experiment: $\Gamma_{\text{exp}} = 4.6\ \text{cm}^{-1}$.[54] To calculate the total frequency shift it is also necessary to take into account the electromagnetic component of the shift $\Delta\omega_{\text{el}} = -2\ \text{cm}^{-1}$ (Ref. 35) owing to the interaction of the dipole of the CO molecule with its image, as well as the frequency shift owing to the interaction of the vibrations of the C=O bond with the vibrations of the CO molecule as a whole relative to the surface $\Delta\omega_{\text{ph}} = 33 \pm 6\ \text{cm}^{-1}$.[56] From here the total shift $\Delta\omega_{\text{tot}} = -67 \pm 6\ \text{cm}^{-1}$,[17,55] which is also in good agreement with experiment: $\Delta\omega_{\text{exp}} = -60 \pm 10\ \text{cm}^{-1}$.[57,76]

The formulas (3.38), (3.40), and (3.41) were derived in the quasiadiabatic limit, when $\Delta \gg \omega_0$. As the molecule moves away from the surface a transition occurs from the quasiadiabatic limit to the strong nonadiabatic limit $\Delta \ll \omega_0$. The formulas describing this transition were derived in Ref. 48. It follows from these formulas that in the quasiadiabatic limit ($\Delta \gg \omega_0$) $\Gamma \sim \Delta^{-2}$, $\Delta\omega \sim \Delta^{-1}$, if $|\varepsilon_a - \varepsilon_F| \ll \Delta$. In the opposite limit ($\Delta \ll \omega_0$) $\Gamma \sim \Delta$, $\Delta\omega \sim \Delta^2$. In this limit polaron narrowing of the electronic level must be taken into account. The theory of polaron narrowing can be constructed by analogy to the theory of the image potential for the fluctuation charge of the adatom.[58] As the distance from the surface increases the width Δ decreases rapidly, so that for small distances between the admolecules and the surface Γ varies more rapidly than $\Delta\omega$, while at a large distance the opposite assertion holds. The dependence of Γ and $\Delta\omega$ on the distance d up to the surface for the case of vibrations of the C=O bond with adsorption of CO on the Ni(111) surface is presented in Fig. 5. One can see from the figure that Γ and $|\Delta\omega|$ have a sharp maximum when the electronic level of the admolecule crosses the Fermi level.

We note that the crossing of the Fermi level by the electron resonance of the admolecule is a fundamental concept, employed for describing diverse surface phenomena, such as diffusion,[59] attachment,[60] adsorption,[61] desorption,[62] scattering of atoms by a surface,[63] restructuring in the adsorbed layer,[64] etc.

The nonadiabatic nature of the motion of the electrons leads not only to damping of the vibrations, but also adds an imaginary component to the dynamic dipole moment, i.e., $\mu = \mu_1(1 + i\omega\tau)$, where μ_1 is the real component of the dynamic dipole moment and $\omega\tau$ is the nonadiabaticity parameter.[8] The polarizability of the adatom is determined by the expression

$$\alpha(\omega) = \alpha_e(\omega) + 2\mu^2\omega_0(\omega^2 - \omega_0^2 + i\omega\gamma)^{-1}, \tag{3.42}$$

where α_e is the electronic part of the polarizability and γ is the damping parameter for the vibrations. In the Anderson-Newns model[8]

$$\alpha_e(\omega) = -\bar{\mu}^2(\rho_a(\varepsilon_F) + i\pi\omega\rho_a^2(\varepsilon_F)), \tag{3.43}$$

$$\gamma = 2\pi\omega(\rho_a(\varepsilon_F)\,\delta e)^2, \tag{3.44}$$

$$\mu_1\tau = -\pi\bar{\mu}\rho_a^2(\varepsilon_F), \tag{3.45}$$

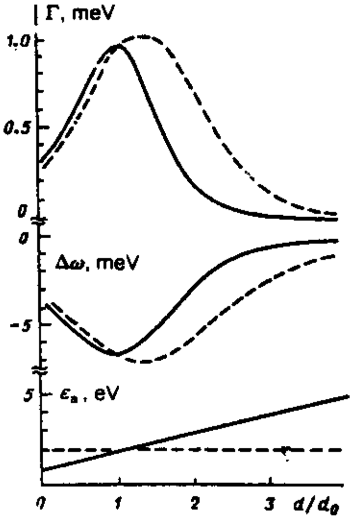

FIG. 5. The linewidth Γ, the frequency shift $\Delta\omega$, and the position of the electronic level ε_a for C=O vibrations in the case of adsorption of CO/Ni(111) as functions of the distance between the molecule and the surface.[17] For the solid lines $\varepsilon_a(d) = \text{const}$; for the broken lines $\varepsilon_a(d) = \varepsilon_A(d_0) + a(d/d_0 - 1)$; $a = 1$ eV.

where $\bar{\mu} = er_0$, r_0 is the distance between the adatom and the plane of the mirror image, $\rho_a(\varepsilon_F)$ is the electronic density of states for the adatom, and $\delta\varepsilon$ is the displacement of the electronic level of the adatom accompanying a shift in the adatom from the position of equilibrium by an amount $Q_0 \doteq (1/2m\omega_0)^{1/2}$. The shape of the spectral line is determined by the expression[8]

$$L(\omega) = V - \operatorname{Im}\alpha(\omega) = 2\frac{\omega_0\mu_1^2(1-xy)^2}{\omega\gamma(1+x^2)}, \qquad (3.46)$$

where $x = (\omega^2 - \omega_0^2)\gamma\omega$, and $y = \omega\tau$. For vibrations of the C=O bond accompanying adsorption of CO on the Cu(100) surface the predicted line shape has an appreciable asymmetry with a low-frequency wing.[8] Experimentally, however, a weaker asymmetry in the opposite direction is observed.[54] According to Ref. 54 the main reason for the difference lies in the fact that in the theory an isolated chemisorbed molecule is studied and the lateral interactions between molecules are ignored. In the general case this interaction leads to strong transfer of intensity to high-frequency modes owing to the dipole-dipole interaction.[76] Another method for checking the electron-hole mechanism for damping is associated with the isotopic effect. According to the formula (3.38) the linewidth is inversely proportional to the reduced mass. For the $c(2\times2)$ structure the difference in the linewidth for $^{12}C^{16}O$ and $^{13}C^{18}O$ with isotopic purity exceeding 90% equals 0.3 cm^{-1}, which falls within the resolution of the experiment. At the present time, however, it is not possible to separate the dipole-dipole interaction; isotopic impurities lead to additional inhomogeneous line broadening of ~ 1 cm^{-1}, masking the isotopic effect.[54]

The strongly asymmetric line shape, described by the formula (3.46), was observed for the wagging vibrations of H on the W(100) surface with the help of IR spectroscopy with coverage $\theta = 2$.[65] For the vibrations of H on the W(100) surface three modes with the frequencies 645 cm^{-1} (wagging), 950 cm^{-1} (asymmetric), and 1060 cm^{-1} (symmetric) are observed. It follows from symmetry that of all the fundamental modes only the symmetric mode can be observed in IR spectroscopy. The first overtone at the wagging frequency $\omega = 2\omega_0$ can, however, be observed. The nature of the formation of the overtone peak was discussed in Ref. 66. It was shown that the form of the overtone is also determined by the formula (3.46). The experimental and theoretical data are compared in Fig. 6. The parameters of the theory were determined from analysis of the experimental data (Table III). The experimental data obtained provide evidence for the fact that the damping of the wagging vibrations of H on the W(100) surface is determined by electron-hole mechanisms. The absence of an isotopic effect, which was observed in Ref. 65, could be linked, as in the case of the system CO/Cu(100), with isotopic disorder, which leads to inhomogeneous line broadening. The strong damping of the wagging vibrations of H on the W(100) surface is associated with the interaction of the hydrogen orbital with the surface states. According to calculations,[67] states with d_{xy} symmetry lie near ε_F (Fig. 7). These states do not participate in the formation of a bond ($V_{ak} = 0$), but they do make a large contribution to the relaxation rate ($V'_{ak} \neq 0$).

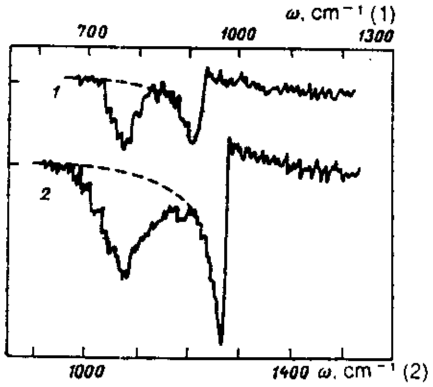

FIG. 6. The vibrational spectra of D (1) and H (2) atoms adsorbed on W(100). The solid lines show the experimental data of Ref. 65 and the broken lines are theoretical curves from Refs. 65 and 66.

TABLE III. Damping parameters for vibrations of H and D on W (100).[65]

Atom	ω, cm^{-1}	γ, cm^{-1}	ωτ
H	1270	26	0.44
D	915	22	0.46

3.4. Intermode energy transfer. An adsorbed atom has the three degrees of freedom, so that because of anharmonicity of the potential well in which the adatom moves energy transfer between different vibrational modes is possible. Taking into account the interaction between two modes A and B only the energy of mode A can be transferred to mode B, while the excess energy $\Delta\omega = (\omega_A - \omega_B)$ is transferred to phonons or electron-hole pairs of the substrate. For example, the calculation of Ref. 8 for S and O atoms adsorbed on nickel showed that the rate of energy transfer between the transverse and longitudinal modes equals at room temperature $\Gamma \approx (0.5\text{–}5)\times10^{-2}\,\omega_0$. An analogous result was also obtained for the system H/W(100).[69] In this case Γ depends strongly on the temperature.[69] Thus for $\omega_A > \omega_B$

$$\frac{\Gamma(T)}{\Gamma(0)} = 1 + n(\omega_B) + n(\omega_A),$$

while for $\omega_A < \omega_B$

$$\frac{\Gamma(T)}{\Gamma(0)} = n(\Delta\omega) - n(\omega_A).$$

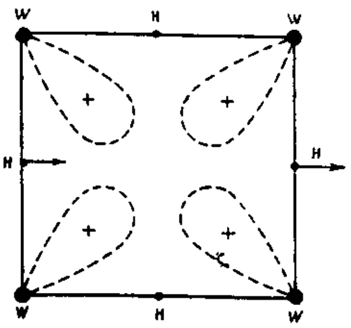

FIG. 7. A schematic diagram of the surface electronic states (broken lines) with which an H atom interacts under conditions of wagging vibrations. These states have d_{xy} symmetry (the z axis is perpendicular to the surface) and do not participate in the formation of a bond between hydrogen and tungsten.

The last process is possible only for $T>0$. In the case of a diatomic molecule the relaxation of intramolecular vibration by means of excitation of vibrations of the molecule as a whole can sometimes be significant. This relaxation mechanism was studied in Ref. 70.

If the interaction between vibrational modes is strong, then perturbation theory cannot be employed. A numerical calculation,[71] performed on the basis of classical mechanics, showed that in this case the motion of the adparticles becomes stochastic over a time $\tau \approx 10^2 \omega_0^{-1}$. In the case of strong coupling separate modes, strictly speaking, cannot be separated, and a two- or three-dimensional Schrödinger equation must be solved. This situation possibly occurs in the system H/Ni.[72] Thus the rate of energy transfer between the vibrational modes can be of the same order as the rate of energy transfer between the local mode and the substrate. It is important to note that in this process, as in the energy transfer studied below between neighboring admolecules, vibrational excitation remains within the adsorbed layer.

4. DYNAMIC INTERACTION BETWEEN ADSORBED MOLECULES

If two identical molecules are adsorbed on the surface of a crystal at the points $\mathbf{r}_1$ and $\mathbf{r}_2$, then they interact with one another with some energy $E_{\text{int}}(\mathbf{r}_1,\mathbf{r}_2)$. The main mechanisms of interaction between adsorbed molecules—direct, indirect, electrostatic (dipole-dipole), and elastic—are described in detail in Ref. 73. This interaction leads to two effects. First, the frequency of the local vibrations of the admolecule in the field of the other molecule is shifted by an amount

$$\Delta\omega \approx Q_0^2 \left(\frac{\partial^2 E_{\text{int}}}{\partial Q_1^2}\right)_{Q_1=Q_2=0}. \tag{4.1}$$

Second, the frequencies are split: $\omega_{\pm} = \omega_0 + \Delta\omega \pm \beta$, where

$$\beta = Q_0^2 \left(\frac{\partial^2 E_{\text{int}}}{\partial Q_1 \partial Q_2}\right)_{Q_1=Q_2=0}. \tag{4.2}$$

If one admolecule is excited while the other is not, then the quantity $\tau = \beta^{-1}$ determines the transfer time from the first admolecule to the second one.

The formulas (4.1) and (4.2) give the adiabatic contribution to the interaction of oscillators. In addition there exist nonadiabatic corrections, owing to the delay in the response of the substrate to the vibration of the admolecule. Such a nonadiabatic interaction in the asymptotic limit ($R \to \infty$, where R is the distance between the molecules) can be stronger than the adiabatic interaction. Nonadiabatic interaction has been studied for electrostatic[12,74] and indirect[75] interaction mechanisms.

If a film with a defective structure is adsorbed on the surface of a crystal, then the interaction between the adparticles leads to inhomogeneous broadening of the vibrational line (see Sec. 5). If, however, the film is ordered, then dispersion of the vibrations appears owing to the interaction, i.e., the component of the wave vector $\mathbf{q}_{\parallel}$ parallel to the surface depends on the frequency of the vibrations ω. For example, for a simple square lattice of adatoms

$$\omega^2(\mathbf{q}_{\parallel}) = (\omega_0 + \Delta\omega)^2 + 4\beta\omega_0(\cos q_x a + \cos q_y a), \tag{4.3}$$

where a is the lattice constant. The vibrational dispersion can be measured by the method of electron energy losses (EELS) with angular resolution. The evolution of the dispersion characteristics as the degree of coverage θ of the substrate changes is especially interesting. However the restructuring of the surface often makes the main contribution to the change in the vibrational frequencies as the coverage θ changes. We note that the wave vector of infrared photons $q \ll 2\pi/a$, so that owing to the law of conservation of momentum only phonon modes with $q_{\parallel} \approx 0$ are observed in the IR spectroscopy method.

The energy of the electrostatic interaction of admolecules has the form[73]

$$E_{\text{int}} = 2\tilde{\mu}(Q_1)\,\tilde{\mu}(Q_2)\,R^{-3}, \tag{4.4}$$

where $\tilde{\mu}$ is the dipole moment formed by the charged adatom together with its image. Using the expressions (4.1) and (4.2) gives for the transverse vibrations

$$\Delta\omega_{\perp} \approx 2Q_0^2 \frac{\partial^2 \mu(Q)}{\partial Q^2} E_{\text{int}}, \tag{4.5}$$

$$\beta_{\perp} \approx \left(\frac{\mu}{\tilde{\mu}}\right)^2 E_{\text{int}}, \tag{4.6}$$

where μ is the dynamic dipole moment, while for longitudinal vibrations

$$\Delta\omega_{\parallel} \approx -\beta_{\parallel} \approx 12\left(\frac{Q_0}{R}\right)^2 E_{\text{int}}. \tag{4.7}$$

It follows from here that the electrostatic interaction is strongest for longitudinal vibrations of admolecules with a large static dipole moment $\tilde{\mu}$, as, for example, for the system Cs/W(100). We note that $\beta_{\perp} \neq 0$ even when $\tilde{\mu} = 0$. The electrostatic interaction plays the main role in adsorption of CO on Cu(100).[76,77] In calculating the susceptibility in this case the screening arising owing to the electronic polarizability of the molecules must be taken into account.

In the infrared region the susceptibility of an isolated molecule equals[76]

$$\alpha_A(\omega) = \alpha_e(\omega) + \alpha_i\omega_A^2[\omega_A^2 - \omega(\omega + i\gamma)]^{-1}, \tag{4.8}$$

where α_e and α_i are the electronic and ionic polarizabilities. Let a molecule with the dipole moment $\tilde{\mu}$ and located at the point $\mathbf{R}_1$ produce at the point $\mathbf{R}_2$ the field $E(\mathbf{R}_2) = -U(\mathbf{R}_2 - \mathbf{R}_1)\mu(\mathbf{R}_1)$, where $U(R) \sim R^{-3}$. Then a Fourier transform of the equation

$$\tilde{\mu}(\mathbf{R}_i) = \alpha_A\left[E(\mathbf{R}_i) - \sum_{i \neq j} U(\mathbf{R}_i - \mathbf{R}_j)\,\tilde{\mu}(\mathbf{R}_j)\right], \tag{4.9}$$

gives

$$\alpha(\omega, \mathbf{q}) = \tilde{\mu}E^{-1} = \alpha_A(1 + \alpha_A\tilde{U}(q))^{-1}, \tag{4.10}$$
$$\tilde{U}(\mathbf{q}) = \sum_j \exp(i\mathbf{q}\mathbf{R}_j)\,U(\mathbf{R}_j).$$

The expression[76] for the reflecting power of the surface follows from here (in the limit $\gamma \to 0$):

$$\delta R \sim \operatorname{Im}\alpha(\omega, 0) = \frac{\pi\alpha_i\omega_A^2}{2\omega_0(1 + \alpha_e\tilde{U})^2}\,\delta(\omega - \omega_0), \qquad .1)$$

where the frequency shift is determined by the formula

$$(\omega_0\omega_A^{-1})^2 = 1 + \alpha_i\tilde{U}(0)[1 + \alpha_e\tilde{U}(0)]^{-1}. \tag{4.12}$$

For the system CO/Cu(100) calculations give $\alpha_e\tilde{U}(0) \approx 1$,[76] i.e., the screening owing to the polarizability of the molecules is significant. For this system the dipole-dipole interaction explains the observed dispersion ~ 40 cm^{-1},[52] while the contribution of the indirect interaction is small.[78]

The indirect interaction has the following asymptotic form[73]

$$E_{\text{int}} \sim f(Q_1)f(Q_2)\cos(2k_F R)R^{-5}, \tag{4.13}$$

where the function $f(Q)$ is determined by the interaction of the admolecule with the substrate owing to overlapping of the orbitals of the molecule and substrate atoms. If the Fermi level crosses the band of surface states, then $E_{\text{int}} \sim \cos(k_F R)/R^2$,[79] i.e., in this case the range of the indirect interaction is greater than that of the dipole-dipole interaction. The indirect interaction is the dominant interaction for adsorption of H and O on the surface of transition metals.[73,80] Calculations[14] for the system H/W(100) give $\Delta\omega_\perp \approx \beta_\perp \approx 40\,\text{cm}^{-1}$ and $\Delta\omega_\parallel \approx \beta_\parallel \approx 400\,\text{cm}^{-1}$. In an experiment for the system H/Pd(100) with $\theta = 1$ the shift $\Delta\Omega = 28$ cm^{-1} was observed.[81] Finally, the elastic interaction energy between the adatoms S and O on Ni(100) was calculated in Ref. 68. It gives the value $\Delta\omega_s = 8$ cm^{-1}.

The picture of dispersion described above is valid only for small displacements of adatoms from their position of equilibrium, when the finiteness of the height of the potential relief along the surface and the nonlinearity of the interaction between the molecules can be neglected. The nonlinearity of the interaction could play an important role for transverse vibrations of H on W(100) with coverage $\theta = 2$. For these vibrations the unusually large linewidth $\Gamma \approx 100$–120 cm^{-1} has been observed with the help of IR spectroscopy.[82] Such a large width cannot be associated with either inhomogeneous broadening or excitation of electron-hole pairs or phonons in the substrate. The frequency shift and spectral-line narrowing accompanying a change in the isotopic composition of the adfilm indicates that there is a strong dynamic interaction between adsorbed hydrogen atoms. While the linear interaction between oscillators leads to a frequency shift, the nonlinearity of the interaction can lead to line broadening. The nature of the dynamic interaction between hydrogen atoms is not clear at present. The dipole-dipole interaction cannot explain the change in the spectral lines accompanying isotopic substitution and is too weak to explain the observed frequency shift. The elastic interaction must be small because of the smallness of the mass of H as compared with the mass of W. Other alternatives are diffusion and indirect interaction. We note that a large width of the optical peaks $\Gamma \approx 160$–200 cm^{-1} is observed for vibrations of hydrogen in transition-metal alloys.[83] It is possible that broadening of the optical peaks for vibrations of a hydrogen atom in the bulk and at the surface is of the same nature.

For large amplitudes of longitudinal vibrations there always exist, in addition to delocalized modes with dispersion $\omega(q_\parallel)$, modes that are localized along the surface. For example, in the case of a one-dimensional chain of adatoms, which is described by the well-known sine-Gordon equation, the local modes correspond to bionic (breather) solutions of the equations.[84] As the energy of the vibrations increases further the bion breaks up into a kink-antikink pair and a defect appears in the structure of the adfilm. It would, of course, be of great interest to observe such bionic modes experimentally.

5. INHOMOGENEOUS LINE BROADENING

Inhomogeneous line broadening is caused by the difference in the local environment of absorbing adsorbed particles occupying different sites on the surface.

The case of adsorption on a uniform surface, when the change in the local environment is associated with a change in the number of neighboring adsorbed particles, has been studied in greatest detail theoretically.[76] Let the adlayer consist of particles A and B, which are distributed randomly over adsorption sites. In the case of isotopic disorder A and B represent different isotopes of the same element. If, however, A is an admolecule and B is a vacancy, then we obtain a description of structural disorder. If the adparticles do not interact with one another, then the reflecting power equals

$$\Delta(\omega) = c_A\Delta_A(\omega) + c_B\Delta_B(\omega), \tag{5.1}$$

where c_A and c_B are the concentrations of molecules of the type A and B, and $\Delta_j(\omega) \sim \operatorname{Im}\alpha_j(\omega)$, where $j = $ A or B. A method for calculating the susceptibility $\alpha(\omega)$ in the coherent potential approximation (CPA) for a mixture of molecules interacting by the dipole-dipole mechanism is described in Ref. 76. In the CPA it is assumed that all adsorption sites are filled with identical particles with "average" susceptibility $\alpha_0(\omega)$, determined from the equation

$$\alpha_0 = \sum_{j=\mathrm{A,B}} c_j\alpha_j \left[1 + (\alpha_j - \alpha_0)\int \frac{d^2q_\parallel\,\tilde{U}(q_\parallel)}{S(1 + \alpha_0\tilde{U}(q_\parallel))}\right]^{-1}, \tag{5.2}$$

where S is the area of the surface Brillouin zone and $\tilde{U}(q)$ is the Fourier component of the interaction potential. The line shape is proportional to the imaginary part of the susceptibility

$$L(\omega) \sim \operatorname{Im}\alpha(\omega) = \operatorname{Im}[\alpha_0(\omega)(1 + \alpha_0(\omega)\tilde{U}(0))^{-1}]. \tag{5.3}$$

Calculation[56] of the reflecting power of an adlayer consisting of the isotopic mixture A $= {}^{12}\mathrm{C}^{16}\mathrm{O}$ and B $= {}^{12}\mathrm{C}^{18}\mathrm{O}$ with adsorption on Cu(100) shows that as the ${}^{12}\mathrm{C}^{16}\mathrm{O}$ concentration decreases the width of the high-frequency peak increases. In particular, for a mixture with $C_A = 0.5$ the increase equals 1 cm^{-1}, which is in good agreement with experiment.[76] An interesting effect is observed in the case of isotopic disorder—the intensity of the absorption of the low-frequency peak B decreases and the intensity of the high-frequency peak A increases as the interaction between the molecules increases. This is linked with the fact that owing to the dipole-dipole interaction a large part of the intensity of the absorption is transferred from the low-frequency peak to the high-frequency peak. For $\omega \approx \omega_B$ the molecules A emit more energy than they absorb. We note that for isotopic disorder the theory predicts an asymmetric line shape with a low-frequency wing.

Experimental and theoretical[76] data on the IR spectra for the isotopic mixture ${}^{12}\mathrm{C}^{16}\mathrm{O}/{}^{12}\mathrm{C}^{18}\mathrm{O}$ with adsorption on Cu(100) and complete filling of the (2×2) structure are

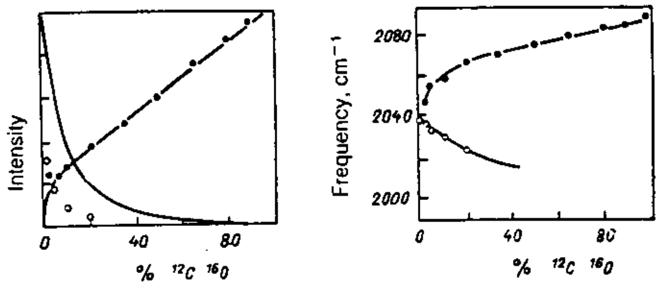

FIG. 8. The positions and intensities of the absorption peaks for $^{12}C^{16}O/^{12}C^{18}O/Cu(100)$ and coverage corresponding to a $c(2\times2)$ structure as a function of the $^{12}C^{16}O$ content.[76] The dots are the experimental points and the solid lines are the computed dependences.

presented in Fig. 8. One can see that the theory is in very good agreement with experiment.

In Ref. 76 the CPA was employed to calculate the absorption spectrum for a structurally disordered monolayer of CO with CO adsorbed on Cu(100). It was assumed that the $^{12}C^{16}O$ molecules are randomly distributed over the sites of a $c(2\times2)$ lattice. In this case the shape of the spectral line is also asymmetric and has a low-frequency wing. The width of the peak increases continuously as the coverage decreases right down to very small values. This is a consequence of the long-range nature of the dipole-dipole interaction.

With a partial monolayer of $^{12}C^{16}O$ and adsorption on Cu(100) a positive shift of the frequency of C═O vibrations from 2077 cm^{-1} with low coverage up to 2068 cm^{-1} with complete coverage of the $c(2\times2)$ structure is observed experimentally; that is, the total shift equals 9 cm^{-1}, which does not agree with the predictions of CPA,[76] according to which the shift should equal $\sim$43 cm^{-1}. This is linked with the fact that there exists a "red" shift of $\sim$30 cm^{-1} owing to the change in the chemisorption bond (chemical shift). Good agreement between theory and experiment was obtained[76] for a partial monolayer of CO with adsorption on Ru(100). This agrees with the fact that when CO is adsorbed on transition metals a large ($\sim$40 cm^{-1}) positive frequency shift, due to the dipole-dipole interaction, is observed. At the same time when CO is adsorbed on precious metals Ag, Au, and Cu a negative frequency shift is observed, i.e., in this case the chemical shift predominates.

In the case when the surface is uniform inhomogeneous broadening is also possible with almost complete coverage of the surface with adsorbed particles of the same kind, if the adsorption layer consists of ordered domains. Inhomogeneous broadening appears in this case owing to variation of the local environment of the particles located on domain walls.

Other obvious and important reasons for inhomogeneous broadening are nonuniformity of the surface itself, presence of different defects on a uniform surface, or presence of impurities on the surface. In the last case the shape of the line is sensitive to the method employed to prepare the surface.

Thus the shift, broadening, and asymmetry of the line shape are a consequence of the change in the local environment of absorbing adsorbed particles. At the present time these effects have been studied in detail only in the case of changes in the local environment owing to a change in the number of neighboring adsorbed particles.

6. DEPHASING OF VIBRATIONS

According to the experimental data the line shape of C═O vibrations with adsorption of CO on Pt(101) (Ref. 85) and Ni(111) (Ref. 86) is strongly temperature-dependent. This dependence cannot be related with multiphonon relaxation, the probability of which is negligibly small for these systems ($\omega_0/\omega_m \gg 1$). Damping owing to excitation of electron-hole pairs gives a virtually temperature-independent line shape. Thus it is natural to suppose that the temperature dependence of these vibrational lines is associated with phase relaxation. For example, in the case of anharmonic coupling of high-frequency vibrations A with low-frequency vibrations B purely phase relaxation of high-frequency vibrations is due to the random modulation of their frequency with low-frequency modes; this is the basis for the exchange model.[87–90] In the case of a diatomic molecule the mode A is related with intramolecular vibrations, while the mode B can be related with vibrations of the molecule as a whole. The Hamiltonian describing the exchange model has the form[89]

$$H = \omega_a a^+ a + \omega_b b^+ b + \sum_k \omega_k b_k^+ b_k + \delta\omega a^+ a b^+ b$$
$$+ \sum_k (V_k b^+ b_k + \text{h.c.}), \tag{6.1}$$

where a^+, b^+, and b_k^+ are boson operators creating a phonon of modes A and B and a substrate phonon. We note that the operator $n_a = a^+ a$ commutes with the Hamiltonian, i.e., the energy of the mode A is conserved. At the same time the mode B can exchange energy with the substrate, so that the number of quanta of mode B changes with time, which leads to random modulation of the frequency of vibrations of the high-frequency mode A. The lowest order of perturbation theory gives[89]

$$\Delta\omega = \delta\omega \bar{n}_b, \tag{6.2}$$

$$\Gamma = 2(\delta\omega)^2 n_b (1 + n_b) \eta_B^{-1}, \tag{6.3}$$

$$\eta_B = 2\pi \sum_k |V_k|^2 \delta(\omega - \omega_k), \quad n_b = [\exp(\beta\omega_b) - 1]^{-1}. \tag{6.4}$$

It follows from these formulas that $\Delta\omega = \Gamma \sim \exp(-\beta\omega_b)$ as $T \to 0$. The formulas are valid when $\eta_B \gg \delta\omega$. A more general solution of the problem is given in Refs. 88 and 90. At high temperatures classical approaches, in particular, Langevin's equation, can be employed to describe phase relaxation processes. In this case the classical analog of the Hamiltonian (6.1) has the form[89]

$$\ddot{x}_a + \omega_a^2 x_a + \alpha x_a x_b^2 = 0, \tag{6.5}$$

$$\ddot{x}_b + \omega_b^2 x_b + \alpha \frac{m_a}{m_b} x_a^2 x_b + \eta_b \dot{x}_b = f(t), \tag{6.6}$$

where $f(t)$ is a random force with $\langle f \rangle = 0$ and the correlation function

$$\langle f(t) f(0) \rangle = 2\eta_b k_B T m_b^{-1},$$
$$\alpha = 2m_b \omega_b \omega_a \delta\omega$$

where $a = 2m_b \omega_b \omega_a \delta\omega$.

The exchange model has been used for analyzing the spectral data for vibrations of the C═O bond with adsorption of CO on Ni(111).[88–90] For adsorption of CO on

Ni(111) at sufficiently low temperatures a $c(4\times 2)$ structure, corresponding to coverage $\theta = 0.5$, was observed first. All CO molecules in this case are in a bridge position. Longer exposures give a $(7/2\times 7/2)R\ 19°$ $(\theta = 0.57)$, structure with every fourth molecule in the position on top of a surface atom, while the remaining molecules are in the bridge position. For molecules in the on top position a large part of the absorption peak is associated with radiation transfer from the molecule in the bridge position owing to the dipole-dipole interaction (see Sec. 5). Therefore the decrease in the width and position of the absorption peak of the molecule in the bridge position also affects the high-frequency peak.

The experimental and theoretical[88] temperature dependences of the width and position of the absorption peak for C=O vibrations with adsorption in the bridge position on the Ni(111) surface are compared in Fig. 9. The values $\omega_b = 220\,\mathrm{cm}^{-1}$, $\eta_b = 37.5\,\mathrm{cm}^{-1}$, and $\delta\omega = 34.4\,\mathrm{cm}^{-1}$ were employed in the calculation. The agreement between theory and experiment is very good. For low temperatures the low-frequency mode is frozen, so that $\Delta\omega$ and Γ are virtually independent of T. It follows from cluster calculations[91] that the frequency of frustrated rotation $\omega_{\mathrm{rot}} = 184\,\mathrm{cm}^{-1}$, while the frequency of frustrated translation $\omega_{\mathrm{tr}} = 76\,\mathrm{cm}^{-1}$, i.e., the frequency ω_b is close to ω_{rot}. According to Ref. 88, for pure rotations $\eta_{\mathrm{rot}} = 40\,\mathrm{cm}^{-1}$, which also agrees with the value employed for η_b. From here it can be concluded that phase relaxation in the case under study is associated with the interaction of high-frequency vibrations with frustrated rotations. For CO molecules in the on top position the observed temperature dependence of Γ and $\Delta\omega$ was weaker; this is attributable to the lower value of $\delta\omega$ in this case.

Another example are the transverse vibrations of H with frequency $\omega_0 = 2097\,\mathrm{cm}^{-1}$ in a hydrogen film $(\theta = 1)$ adsorbed on Si(100)-(2×1).[92] The theoretical and experimental temperature dependences of the linewidth are compared in Fig. 10. The calculation was performed by the method of molecular dynamics for a cluster consisting of 44 atoms with Langevin boundary conditions. It follows from the calculation that $\tau^{-1} \lesssim 10^{-2}\,\mathrm{cm}^{-1} \ll \Gamma$. The experimental dependence is approximated well by a straight line, whose slope equals $680 \pm 50\,\mathrm{cm}^{-1}$, which agrees well with the theoretical frequency of bending vibrations of the H=Si bond. From here it can be concluded that dephasing of vibrations of H=Si perpendicular to the surface is due to interaction of these vibrations with frustrated rotations of the H=Si bond. An analogous situation also occurs for the system Ge(100)—(2×1)—H, for which at temperatures $T > 250$ K the dependence of the logarithm of the linewidth on the inverse temperature can also be approximated well by a straight line with slope $\sim 500\,\mathrm{cm}^{-1}$, which agrees with the frequency of frustrated rotations $\sim 550\,\mathrm{cm}^{-1}$.[92]

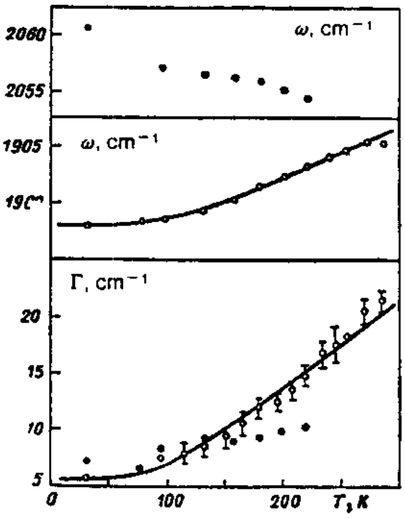

FIG. 9. The position and width of the absorption peaks of C=O vibrations for adsorption on Ni(111).[88] The dots correspond to the bridging and terminal positions of CO; the solid lines are the computed dependences.

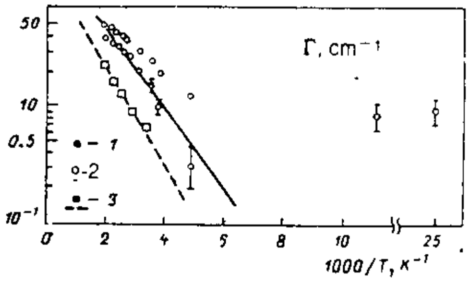

FIG. 10. The linewidth of H=Si vibrations for the system Si(100)-(2×1)H.[92] 1) Experiment; 2) experiment after the contribution of inhomogeneous broadening ($9\,\mathrm{cm}^{-1}$) is subtracted out; 3) calculation.

Dephasing of vibrations can also occur owing to elastic "collisions" with substrate phonons. The corresponding calculation for vibrations of CO as a whole with adsorption on Ni(111) was performed in Ref. 93. In this case the interaction Hamiltonian responsible for dephasing has the form $H_{\mathrm{int}} = cQ_a^2 Q_2^2$, where c is a constant Q_a is the coordinate of the surface atom, and Q_2 is the coordinate of the vibrations of the local mode of the admolecule. It was found that dephasing makes a contribution of $\approx 1\,\mathrm{cm}^{-1}$ to the linewidth, which is significantly less than the experimentally observed width of $\approx 15\,\mathrm{cm}^{-1}$, associated with decay of vibrations owing to anharmonicity. Analogously for the H/W(100) system dephasing owing to elastic collisions with substrate phonons makes the contribution $\sim 10^{-6}\omega_0$ to the linewidth. It follows from the calculations performed that the dephasing of high-frequency vibrations is efficient if the local phonon density of states of the low-frequency mode has a narrow resonance.

Purely phase relaxation of vibrations of adsorbed particles could also be due to interaction with conduction electrons. This process was studied using the Anderson-Newns model in Ref. 94. It was found that in this case the linewidth $\sim T^3$. Estimates[94] give $\Gamma \approx 20\,\mathrm{cm}^{-1}$ for CO vibrations on Ni(111); this agrees well with experiment.[95]

The dephasing studied above is related with the stochastic character of the motion in a system with many degrees of freedom. Stochastic motion can also occur in systems with a small number of degrees of freedom,[95] in particular, in a system consisting of anharmonically coupled oscillators. In this system with low energy E the vibrations are harmonic. As the energy E is increased the interaction between modes becomes stronger $(H_{\mathrm{int}} \sim E^n,\ n > 3/2)$, and this leads to "beats"—energy exchange between modes. As the energy is increased further above some critical value E_c stochastic motion appears in the system. This effect is described in greater detail in Ref. 95. Here we only note that on stochastization, first of all, the Kolmogorov-Sinaĭ entropy h, characterizing the rate of spreading of the close-lying trajectories of the motion of the system in phase space, grows rapidly and, second, exponential decay of the time correlation function

$$\langle Q_A(t)\,Q_A(0)\rangle \sim \exp\left(-\frac{\Gamma}{2}t\right), \quad \Gamma \sim h, \tag{6.7}$$

appears, which leads to narrowing of the spectral line. This mechanism of dephasing with two-dimensional motion of the adatom (B type absorption) was studied in Ref. 71. It was shown that for the system H/W (100) $\Gamma \sim 10^{-2}\,\omega_0 \approx 10$ cm^{-1}. An obvious way to make the model more complex is to increase the size of a cluster, i.e., to increase the number of nonlinearly coupled modes. With the exception of exotic cases (such as the Fermi-Pasta-Ulam paradox[95]) this lowers the threshold for the appearance of chaos ($E_c > 0$).[95] In so doing taking into account the quantum character of the motion of the system does not qualitatively change the results.

7. THE ROLE OF VIBRATIONAL RELAXATION IN SURFACE DYNAMIC PROCESSES

A great deal of attention is traditionally devoted to the study of elementary dynamic processes on a surface, such as diffusion, adsorption-desorption processes, and the elementary stages of chemical reactions, since these processes play an important role in different areas of physics and chemistry, in particular, in heterogeneous catalysis. Dynamic processes on a surface are described with the help of the method of molecular dynamics or the equations of nonequilibrium thermodynamics (Langevin, Fokker-Planck, and Pauli equations). Theoretical analysis of dynamic processes is possible only if the form of the potential energy surface for the motion of adsorbed particles is known. Information about the form of potential surfaces can be obtained from calculations of the electronic structure of the system substrate + adsorbate and from experiments on scattering of molecular beams by a surface. Both these approaches are currently being intensively developed.[96]

An elementary understanding of the role of vibrational relaxation in dynamic processes can be obtained by studying the process of a particle overcoming the activation barrier. If Langevin's equation or the equivalent Fokker-Planck equation is employed to describe the motion of the particle, then the rate constant of the process, as is well-known,[97] has the form

$$k = A\exp\left(-\frac{E_a}{k_B T}\right), \tag{7.1}$$

$$A \approx \frac{\eta E_a}{k_B T}, \quad \eta < \frac{\omega_* k_B T}{2\pi E_a}, \tag{7.2}$$

$$\approx \frac{\omega_0}{2\pi}, \quad \frac{\omega_* k_B T}{2\pi E_a} < \eta < \omega_*, \tag{7.3}$$

$$\approx \frac{\omega_0 \omega_*}{2\pi\eta}, \quad \eta > \omega_*, \tag{7.4}$$

where E_a is the activation energy, η is the coefficient of friction, ω_0 is the frequency of oscillations near the position of equilibrium, and ω_* is the frequency corresponding to vibration in the "inverted" potential near the activation barrier. The formulas (7.1)–(7.4) were derived in describing the one-dimensional classical motion of a particle along the adiabatic potential energy surface. Analogous results are also obtained in a quantum description based on Pauli's equation.[62] The multidimensional nature of the motion can be taken into account by premultiplying (7.1) by the partition function of the activated complex and dividing by the partition functions of the starting reagents; the typical values of the preexponential factors so obtained for different processes on a surface are tabulated in Ref. 98. If the process is nonadiabatic, then the expression (7.1) must be premultiplied by a transmission coefficient (the transmission coefficient is calculated in Ref. 99).

In the case of surface processes friction is usually weak, so that the limit (7.4), as a rule, is not realized. On the other hand it is also usually difficult to satisfy the condition (7.2), since the parameter $2\pi E_a/k_B T$ is large for activated processes. Thus the condition (7.3), corresponding to applicability of the well-known[23] theory of the transient state (in the one-dimensional case this theory gives $A = \omega_0/2\pi$), is realized most often.

One would expect, however, that the limit of weak friction (7.2) is realized in the case of adsorption of light particles on the surface of metals, when excitation of electron-whole pairs makes the dominant contribution to friction. In this case any change in the electronic structure of the adsystem, for example, accompanying phase transformations[59,100] or the Kondo effect owing to electronic correlations on the adatom,[49] will change η and therefore A also. Since for the electron-hole mechanism of friction $\eta \sim \rho_a^2(\varepsilon_F)$, where $\rho_a(\varepsilon_F)$ is the electronic density of states for the adatom, any change in the electronic density of states $\rho_a(\varepsilon_F)$ will also give rise to a change in A.[59] For example, for a Peierls transition on the surface of a crystal, which apparently occurs when the (100) face of tungsten and molybdenum[101] is restructed, a gap appears in the vicinity of the Fermi level of the substrate and $\rho_a(\varepsilon_F)$ vanishes, so that friction will be determined primarily by the phonon mechanism. As the temperature of the substrate or the density of adatoms at the point when restructuring vanishes increases, the coefficient of friction should increase sharply; this can be observed by measuring experimentally[21] the temperature or concentration dependence of the coefficient of diffusion of light atoms (H, D, Li). The rate of energy transfer owing to the electron-hole mechanism depends on the position of the electronic resonance of the adsorbage relative to the Fermi level; it is maximum when the electronic resonance crosses the Fermi level. Thus by changing the position of the electronic resonance it is possible to control the rate of dynamic processes on a surface. The position of the electronic resonance can be changed by applying an external field, by interaction between adsorbed particles, or if the adparticle moves parallel to the surface with a sufficiently high velocity.[63]

The electron-hole mechanism of energy transfer can play an important role in adsorption[41,60] and desorption[62] of light particles. For example, according to Ref. 41 a hydrogen atom incident on the surface of *Ag* with thermal energy ~25 meV completely loses its energy owing to excitation of electron-hole pairs at a distance ~1–2 Å.

For low-frequency vibrations with $\omega_0 < \omega_m$ the coefficient of friction is determined by single-phonon processes[88,102]

$$\eta_{\rm ph} \approx \xi \frac{m_a}{m_s}\left(\frac{\omega_0}{\omega_M}\right)^3 \omega_0, \tag{7.5}$$

where $\xi \approx 1$ is a numerical coefficient (in particular, for Debye's model $\xi = 3\pi/2$). Calculations show that for low-frequency vibrations with $\omega_0 \ll \omega_m$ the coefficient of friction owing to the electron-hole mechanism can be of the same order as the phonon coefficient of friction.

Under conditions of weak energy transfer between the adfilm and the substrate the adfilm is very sensitive to external perturbations. External excitation of the adfilm, for example, with laser radiation, an electron beam, or accompanying the emission of field-emission current, can transfer the system into a nonequilibrium state. In this case stimulated surface processes—diffusion, desorption, disordering, attachment, etc., whose rate will be appreciably higher than the thermodynamic equilibrium rate—are possible.[103]

In the case of chemical reactions on a surface the energy of the reaction products immediately after the activation barrier is overcome is usually significantly higher than the thermal energy. If the reaction products then leave the surface, this excess energy can be observed experimentally if the evaporation process is much faster than the relaxation processes in the adsorbed layer. The superthermal energy excess has been observed for a number of dynamic processes.[104] It is interesting that the excess energy is often concentrated in the vibrational degrees of freedom.

The examples studied above show that the information about energy exchange between adsorbed particles and the substrate (in particular, the data obtained based on analysis of the vibrational spectra) has a direct bearing on the dynamic processes at the next level of complexity, such as, diffusion, adsorption, desorption, etc.

8. CONCLUSION

Over the last ten years significant progress has been achieved in developing experimental measuring methods and in the theoretical interpretation of the shape of vibrational spectra of adsorbed particles. It has been established that on a surface, just like in other media, aside from the lifetime purely phase relaxation processes as well as inhomogeneous broadening make a significant contribution to the linewidth. This fact shows, on the one hand, the limitations of the method of IR spectroscopy for determining the lifetime and, on the other, that the method is sensitive to structural, chemical, and dynamic properties of the surface. It should be emphasized that the information content of the method of IR spectroscopy is strongly predicated on the development of theoretical models of the shape of vibrational lines. Numerous examples of the theoretical interpretation of experimental results have been presented in this review.

Further progress in experimentation in the field of vibrational spectroscopy is predicated on more detailed and systematic study of line shapes as a function of the temperature, coverage, isotopic composition of the adlayer, and surface defects. Inhomogeneous broadening owing to the defective nature of the surface, the presence of domains on the surface, etc. and being responsible for the often observed nonreproducibility of results even for systems that are ordered from the viewpoint of LEED, must be studied in greater detail experimentally. Inhomogeneous broadening must also be studied theoretically in greater detail.

Natural broadening, owing to relaxation of the populations and purely phase relaxation, is understood qualitatively quite well. In this area of the theory detailed numerical calculations, whose accuracy is comparable to the experimental resolution, must now be performed. At the present few such calculations have been performed, and they are being held back by the lack of reliable data on the potential energy surface for the motion of adsorbed particles.

From the general physical viewpoint it is of interest to study vibrational spectra experimentally and theoretically under conditions of phase transitions in the adlayer, when a strong change in the line shape can be expected. Such studies are only now beginning to appear.

Progress achieved in the measurement and interpretation of vibrational spectra shows that at the present time vibrational spectroscopy is a powerful method for studying surface processes.

We thank A. G. Naumov for useful discussions.

[1)] In what follows the atomic system of units $\hbar = m_e = e^2 = 1$ is employed everywhere.

[2)] It should be noted that when the preexponential factor changes the activation energy of the process changes at the same time, so that it is a quite difficult problem to establish experimentally the change in the rate of the process owing to a change in the coefficient of friction.

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On the origin of anti-absorption resonances in adsorbate vibrational spectroscopy

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We explain the origin of recent observations of anti-absorption peaks in infrared-reflection-absorption spectroscopy (IRAS) of atoms and molecules adsorbed on metal surfaces. It is shown that parallel frustrated translations of adsorbates always give rise to relatively strong anti-absorption peaks in IRAS, even though these modes are dipole-forbidden with respect to a normal electric field. The excitation mechanism is indirect, involving the metal electrons. The practical importance of this result is emphasized.

The study of vibrations in adsorbed molecules is a powerful method to gain insight into the nature of the adsorbate–substrate bond. For example, the frequency of the C–O stretch vibration for CO adsorbed on metallic surfaces decreases with increasing coordination, and from the frequency shift alone it is often possible to deduce the binding sites on the surface. Of particular interest are the low-frequency parallel vibrations, the so-called frustrated translations. The frequencies of these modes reflect the lateral curvature, at the binding sites, of the adsorbate–substrate potential energy surface. This information is of utmost importance for the understanding of many static and dynamic properties of adsorbed layers, e.g. surface diffusion, the nature of adsorbate structures and phase transitions in adsorbed layers. To give an example, it has been shown [1] that domain wall superstructures, which often occur at high coverage in adsorbate systems, are usually stable only because the adsorbates along the domain walls can move away from the substrate symmetry sites in order to lower the total energy.

Vibrations in adsorbed molecules can be studied using infrared-reflection-absorption spectroscopy (IRAS), electron-energy-loss spectroscopy (EELS) or inelastic helium scattering. The last method is particularly suitable for the low-frequency frustrated translations and has been successfully applied to CO on Ni(100), Pt(111) and Cu(100) [2,3]. Until recently, the resolution of EELS was not high enough to resolve parallel frustrated translations for most adsorbates, e.g. CO. However, recently EEL spectrometers with a resolution better than 1 meV have been developed, and in an EELS study by Kisters et al. [4], all the adsorbate vibrational modes for CO on Ir(100) have been detected in off-specular EELS.

In the context of IRAS it has generally been believed that only vibrational modes with a non-zero dynamical dipole moment normal to the surface can be detected. This conclusion was based on the strong screening of the parallel electric field at the surface (see below). But recently, parallel frustrated translations (H on W(100) and on Mo(100)) and frustrated rotations (CO on Cu(100)) have been observed with IRAS. In fig. 1 we reproduce the reflectance spectrum from CO on Cu(100), in the vicinity of the resonance frequency $\Omega \approx 285$ cm^{-1} of the frustrated rotation. Note the peculiar anti-absorption structure associated with this vibrational mode. This result should be contrasted with those of vibrational modes with finite dynamical dipole moments normal to the surface, for which reflection "dips" occur. It is the aim of this work to explain how parallel frustrated translations (and frustrated rotations which also involve some translations) can be excited in IRAS.

Consider an electromagnetic wave incident on a metal surface. It is well known that at IR frequencies

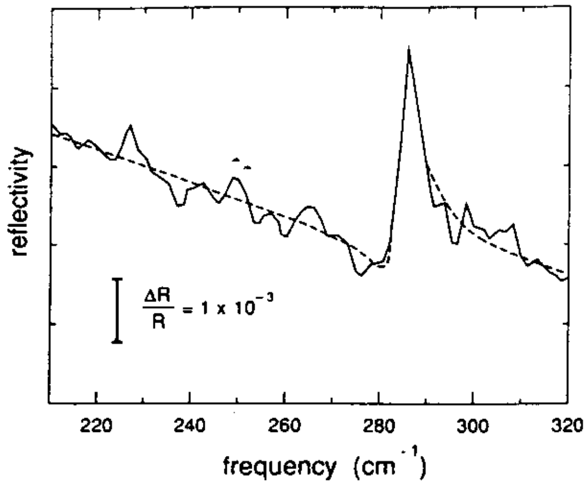

Fig. 1. IRAS spectra in the frequency region of the frustrated rotation for CO on Cu(100). From ref. [6].

(say $\omega \approx 500$ cm^{-1}) the electric field on the vacuum side is almost orthogonal to the surface. This follows from the continuity of $E_\parallel$ at the surface and from the strong screening of the electric field in the metal. It was therefore a surprise when Chabal [5,6] and co-workers observed formally dipole-forbidden (with respect to the surface normal) low-frequency frustrated translations (H on W(100) and Mo(100)) and rotations (CO on Cu(100)) of adsorbates on metallic surfaces. In fact, these modes are observed as strongly as the low-frequency dipole active modes (e.g. the H–W, H–Mo, and CO–Cu stretching vibrations) even though the parallel electric field vector at the surface is reduced by a factor $|E_\parallel/E_\perp| \sim \omega/\omega_p \approx 0.01$ compared with the normal electric field component, and the corresponding IR intensity ratio is reduced by the factor $|E_\parallel/E_\perp|^2 \sim \omega^2/\omega_p^2 \approx 10^{-4}$. A clue to the explanation of these puzzling results followed from the observation that the dipole-forbidden modes observed with IR spectroscopy could not be observed by electron-energy-loss spectroscopy (EELS) (dipole scattering). In EELS, the ratio between the parallel and normal electric field components at the vacuum side of the metal surface is even smaller than in IRAS (see fig. 2), namely $\sim \omega^2/\omega_p^2 \approx 10^{-4}$ and the field intensity ratio $\sim \omega^4/\omega_p^4 \approx 10^{-8}$. However, this difference between IRAS and EELS is not likely to be of any practical relevance since already with IRAS the reduction is strong enough ($\approx 10^{-4}$) to exclude the direct coupling between the adsorbates and the parallel electric field. On the other hand, since $E_\parallel$ is continuous at the surface, the same difference in electric field strength between IRAS and EELS occurs in the surface region inside the metal (see fig. 2). Hence if the excitation of the dipole-forbidden modes is mediated by the metal electrons, then a big difference (by a factor of $(\omega/\omega_p)^2 \approx 10^{-4}$) can be expected between IRAS and EELS. This fact has already been pointed out by Chabal and co-workers (see also refs. [7,8]).

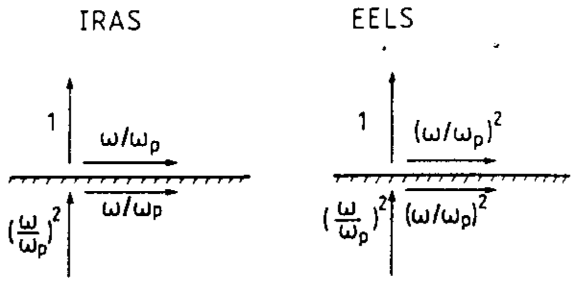

Fig. 2. The relative strength of the normal and parallel electric field vector components at a metal surface in IRAS and EELS. The electric field ratios for IRAS follow directly from the Fresnel formulas for the electric field. In EELS (dipole scattering) the momentum transfer $q_\parallel$ is so large that retardation effects can be neglected, i.e. $cq_\parallel \gg \omega$, and the electric field ratios indicated in the figure from the Fresnel formulas by taking the limit $c \to \infty$.

A second observation which supports the indirect, via the metal electrons, excitation of the dipole-forbidden vibrational modes is the observation of an adsorbate-induced change in broad-band IR reflectivity. This was observed both for CO on Cu(100) [6] and for H on W(100) and Mo(100) [5,9]. Before presenting a quantitative study of this topic let us give a qualitative discussion about the origin of the background absorption and also about how dipole-forbidden adsorbate vibrations can be excited in IRAS. We focus on the three processes shown in fig. 3.

Fig. 3a describes a process where a photon excites an electron from a level $|\alpha\rangle$ below the Fermi surface to a level $|\beta\rangle$ above the Fermi surface. The momentum necessary for this excitation is supplied by the adsorbates and the process results in the IR background discussed above. For a metal film, in the limit $\omega \to 0$, where ω is the frequency of the oscillating electric field, this process gives the adsorbate-in-

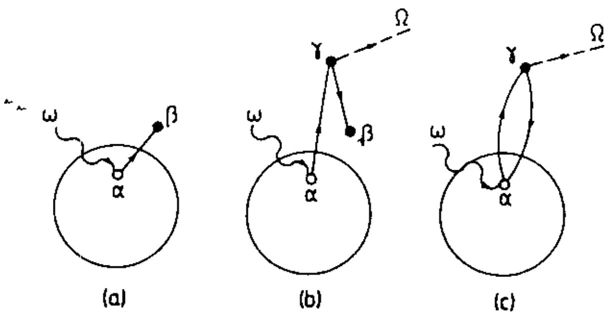

Fig. 3. Elementary processes which contribute to the surface absorptivity.

duced contribution to the dc resistivity of the film.

In fig. 3b, we indicate a process where a photon is absorbed while an electron is excited from a level $|\alpha\rangle$ ($\epsilon_\alpha < \epsilon_F$) to a level $|\gamma\rangle$ ($\epsilon_\gamma > \epsilon_F$). The intermediate state $|\gamma\rangle$ is in general a virtual state, i.e. $\epsilon_\gamma - \epsilon_\alpha \neq \omega$. The momentum needed for this excitation is supplied by the adsorbate. Next, the excited electron scatters inelastically from the adsorbate resulting in a vibrationally excited molecule and an electron in an orbital $|\beta\rangle$ above the Fermi energy ($\epsilon_\beta = \epsilon_\alpha + \omega - \Omega > \epsilon_F$). This process does not give rise to a sharp structure in the reflectance at $\omega = \Omega$ but to an onset at $\omega = \Omega$, i.e. $\Delta R \sim \theta(\omega - \Omega)(\omega - \Omega)$ in the vicinity of $\omega = \Omega$.

We will show that process (c) (fig. 3c) does give rise to a sharp structure at $\omega = \Omega$ and furthermore that the intensity of this structure can be large. In process (c), an electron is excited from a state $|\alpha\rangle$ ($\epsilon_\alpha < \epsilon_F$) to an intermediate and in general virtual state $|\gamma\rangle$ ($\epsilon_\gamma > \epsilon_F$) and $\epsilon_\gamma - \epsilon_\alpha \neq \omega$. Again the momentum needed for this excitation is supplied by the adsorbate. Next, the excited electron scatters inelastically from the adsorbate while exciting the vibration Ω. In contrast to case (b), the electron does not end up in a state $|\beta\rangle$ above the Fermi energy but recombines with its own hole. Energy conservation therefore requires that $\omega = \Omega$, i.e. this process gives rise to a sharp structure at $\omega = \Omega$. In general, the structure is not a Dirac delta function but will be broadened due to coupling between the excited vibrational state and the e–h pair excitations of the metal.

Processes (a) and (c) can be treated in a coherent but semiclassical manner as follows. Consider first a thin metallic film (thickness d) with a layer of adsorbed molecules. Assume that an oscillating electric field $E \sim \exp(-i\omega t)$ acts on the electrons in the film. This induces a collective (drift) motion of the electrons, corresponding to an oscillating current $J = ne\dot{x}$, where x is the electron displacement and n the number of conduction electrons per unit volume. In addition, the adsorbates can perform oscillations parallel to the surface (normal mode coordinate Q). In a semiclassical treatment, the equations of motion for Q and x take the form

$$\ddot{Q} + \Omega^2 Q + \frac{1}{\tau}(\dot{Q} - \dot{x}) = 0\,, \tag{1}$$

$$\ddot{x} + \frac{1}{\tau_B}\dot{x} + \frac{Mn_a}{mnd\tau}(\dot{x} - \dot{Q}) = \frac{e}{m}E\,, \tag{2}$$

where n_a is the number of adsorbates per unit area and m and M the electron and adsorbate mass, respectively. Note that the friction force on the adsorbate motion involves the relative velocity $\dot{Q} - \dot{x}$ between the vibrating adsorbate and the collective motion of the conduction electrons. The last term on the lhs of eq. (2) is the reaction force on the electrons from the friction force acting on the adsorbate. The friction coefficient $1/\tau$ is the damping rate, due to excitation of electron–hole pairs, of the frustrated translation Q. Substituting $E = E(\omega)\exp(-i\omega t)$ in (1) and (2) gives

$$\left(-\omega^2 + \Omega^2 - i\frac{\omega}{\tau}\right)Q(\omega) = -i\frac{\omega}{\tau}x(\omega)\,, \tag{3}$$

$$\left(-\omega^2 - i\frac{\omega}{\tau_B}\right)x(\omega) - i\omega\frac{Mn_a}{mnd\tau}[x(\omega) - Q(\omega)] = \frac{e}{m}E(\omega)\,. \tag{4}$$

If we define the conductivity $\sigma(\omega)$ by

$$-i\omega nex(\omega) = \sigma(\omega)E(\omega)$$

then it follows from (3) and (4) that

$$\sigma(\omega) = ne^2/m \times\left(-i\omega + \frac{1}{\tau_B} + \frac{Mn_a}{mnd\tau}\frac{\Omega^2 - \omega^2}{\Omega^2 - \omega^2 - i\omega/\tau}\right)^{-1}. \tag{5}$$

Hence, if we define an effective surface relaxation time τ_s by

$$\frac{1}{\tau_s}=\frac{Mn_a}{mnd\tau}\frac{\Omega^2-\omega^2}{\Omega^2-\omega^2-i\omega/\tau}, \quad (6)$$

then the conductivity $\sigma(\omega)$ takes the usual form

$$\sigma(\omega)=\frac{ne^2}{m}\frac{1}{-i\omega+1/\tau_{tot}}, \quad (7)$$

where

$$\frac{1}{\tau_{tot}}=\frac{1}{\tau_B}+\frac{1}{\tau_s}. \quad (8)$$

Since $\tau_s \to mnd\tau/Mn_a$ as $\omega \to 0$, it follows that from the study of the variation of the dc resistivity of thin metallic films, as a function of the adsorbate coverage, one can deduce the lifetime τ of the parallel frustrated translation. This topic has been discussed in detail elsewhere [10], where, for example, for CO on Cu(111), dc resistivity data give $\tau \approx 3.9\times10^{-11}$ s. Here we instead focus on the change in the IR reflectance, ΔR, induced by adsorbates on a semi-infinite metallic substrate. It has been shown [11] that for $\omega \gg 1/\tau_B$ and $\omega/\omega_p \gg v_F/c$ the adsorbate-induced change in the reflectivity is given by

$$\Delta R=-\frac{4\omega}{c}\frac{1}{\cos\theta}\,\mathrm{Re}\,\frac{d}{\omega\tau_s}. \quad (9)$$

Substituting (6) in (9) gives

$$\Delta R=-\frac{4Mn_a}{mnc\tau}\frac{(\Omega^2-\omega^2)^2}{(\Omega^2-\omega^2)^2+(\omega/\tau)^2} \quad (10)$$

which is our fundamental result. This equation has been derived earlier using a quantum-mechanical approach [11]. However, the present derivation is simpler and gives a more intuitive understanding of the physics involved.

The reflectance predicted from this formula is shown in fig. 4. For $|\Omega-\omega| \gg 1/\tau$ a uniform background absorption occurs due to excitation of electron–hole pairs – this effect corresponds to process (a) in fig. 3. Centered at $\omega=\Omega$ is an anti-absorption peak, i.e. the reflectance is higher (in fact unity) at resonance $\omega\approx\Omega$ than away from resonance. This has a simple physical meaning: According to (1), $\dot{Q}-\dot{x}=0$ for $\omega=\Omega$, i.e. no relative motion occurs between the vibrating adsorbate and the collective motion of the electron gas, resulting in no energy absorption and unit reflectivity.

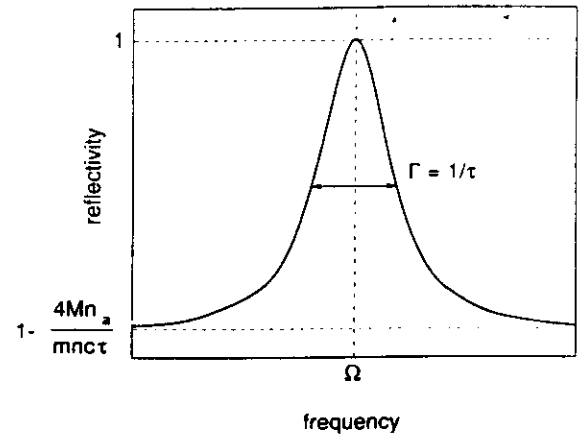

Fig. 4. Theoretical IR reflectance spectra from a surface with adsorbed molecules with frustrated translations with resonance frequency Ω and damping $\Gamma=1/\tau$. The inequality $\omega/\omega_p \gg v_F/c$ is assumed to hold.

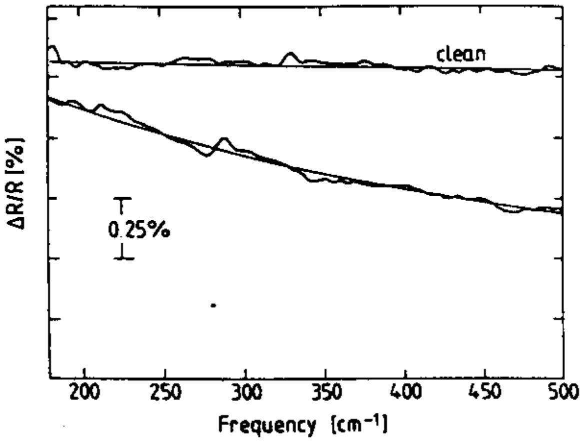

Fig. 5. The IR reflectance of a clean and a CO-covered Cu(100) surface. The CO coverage $\theta=0.15$ and the temperature $T\approx 90$ K. The smooth solid line is discussed in the text. From ref. [6].

Eq. (10) is only valid for $\omega\tau_B \gg 1$ and $\Omega/\omega_p \gg v_F/c$. If these conditions are satisfied, (10) predicts that the background absorption should be ω-independent. But this is not observed in the frequency region 200 cm^{-1} $<\omega<$ 500 cm^{-1} for CO on Cu(100), see fig. 5. The reason is that while the condition $\omega \gg 1/\tau_B \approx 25$ cm^{-1} is well satisfied in the frequency range presented in fig. 5, the other condition $\omega/\omega_p \gg v_F/c$ necessary for the validity of (10) is not satisfied since $v_F/c \approx 0.005$, while $\omega/\omega_p \approx 0.006$ for $\omega=500$

cm^{-1}. However, the absorption background can be analyzed by extrapolating the experiment data in fig. 5 to higher frequencies. The smooth solid curve in fig. 5 is given by

$$\Delta R = -a\frac{\omega^2}{\omega^2+b^2},$$

where $a=9.05\times10^{-3}$ and $b=357\ \mathrm{cm}^{-1}$. Hence $\Delta R\to -a$ as $\omega \gg b$, which must equal $\Delta R = -4Mn_a/mnc\tau$ according to (10). Using this equation with $M=28u$, $n_a=0.023$ Å^{-2} (corresponding to the coverage $\theta=0.15$), $n=8.47\times10^{-2}$ Å^{-3} and $\Delta R=-a$ gives $\tau=2.6\times10^{-11}$ s which is in rather good agreement with the lifetime deduced from dc resistivity data in refs. [10,11], namely $\tau=3.9\times10^{-11}$ s. Hence we conclude that the decrease in IR reflectivity upon CO adsorption is most likely due to the increase in "surface resistivity" and not, as suggested by Hirschmugl et al. to inter or intra-band transitions involving adsorbate-induced electronic surface states.

We are working on an extension of the theory presented above to be valid also when $\omega/\omega_p < v_F/c$. Eq. (9) is based on the Feibelman *d*-parameter formalism [12] for calculating the leading corrections to the Fresnel formulas for the reflectivity of a metal surface. In the present context this corresponds to an expansion to zero order in the parameter $\omega_p v_F/\omega c$. But this expansion parameter is not small (in fact, it is of order unity or larger) at those frequencies where the frustrated translations or rotations occur in adsorbed molecules. We expect that, in an extended theory, the resonance structure in the reflectivity at $\omega\approx\Omega$ will not be perfectly symmetric as in (10) (inverted Lorentzian) but some asymmetry will occur, as observed both for CO on Cu(100) (see fig. 1) and for H on W(100) and Mo(100). Note also that (10) is only valid for a "pure" frustrated translation and must be modified for a frustrated rotation. Nevertheless, we emphasize that the basic physics is contained already in the treatment presented above.

To summarize, we have shown that parallel frustrated translations, which are formally dipole-forbidden with respect to an electric field normal to the surface, will always show up as relatively strong anti-absorption or Fano-like structures in IR absorption spectra. This has two important implications:

(a) IR spectroscopy of adsorbates on metallic surfaces will in general detect all the vibrational modes of adsorbed molecules, an important result contrary to common belief. The so-called "surface selection rule" is therefore wrong in IRAS!

(b) Parallel vibrational modes with zero dynamic dipole moment normal to the surface should always exhibit anti-absorption peaks or strong Fano lineshapes. On the contrary, adsorbate vibrations with non-vanishing dynamical dipole moments normal to the surface, usually give rise to almost Lorentzian-like absorption peaks. Hence, from the nature of the IR absorption spectra it is possible to state directly if a particular absorption peak is due to a vibrational mode with a dynamic dipole moment parallel or normal to the surface. This should be contrasted with EELS where usually only vibrations with a non-vanishing normal dynamical dipole moment are detected under specular scattering conditions, while non-dipole (with respect to the surface normal) excitations can be observed off-specular via impact or resonance scattering.

Finally, we suggest that more IRAS measurements of frustrated translations should be performed on simpler systems than those studied earlier. For example, H on a Cu surface seems to be a good case [13], since Cu is rather free-electron like at low frequencies (no d-bands at the Fermi energy) and no change in reconstruction occurs as a function of H-coverage as is the case for H on W(100) and Mo(100). The latter fact is important since accurate knowledge of the adsorbate-induced background absorption can be obtained only if the clean (reference) surface has the same geometrical structure as the H-covered surface.

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-45-

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Cubic anharmonicity and multiphonon vibrational relaxation of adsorbed molecules

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For a localized vibration of a linearly bonded adsorbate, with a relative high-frequency displacement coordinate q_a, coupled to a substrate mode with displacement coordinate q_s, we propose a new contribution to the linewidth arising from the cubic terms $q_a^2 q_s$ and $q_a q_s^2$ by going to third and higher order in perturbation theory. For third- or higher-order multiphonon processes, this contribution is shown through a specific example to be much more important than the leading-order damping contribution from the term $q_a q_s^n$ $(n>2)$, which has been considered by others.

The main mechanisms of the vibrational relaxation of an atom or a molecule adsorbed on a surface are associated with excitation of electron–hole pairs, and with emission and absorption of phonons. For phonon damping, it has been generally believed that the most important contribution to the linewidth, due to emission of two and three phonons, arises from the terms $q_a q_s^2$ and $q_a q_s^3$ in the anharmonic part of the interaction Hamiltonian. Nevertheless, we show here that, for multiphonon processes of third or higher order, the cubic terms $q_a^2 q_s$ and $q_a q_s^2$ give a much larger contribution to the relaxation (damping) rate than the term $q_a q_s^n$ $(n>2)$ to lowest order in perturbation theory. In fig. 1, we show, for $n=3$, the contributions to the self-energy (which determines the linewidth and frequency shift) of the high-frequency mode from the term $q_a q_s^3$ (fig. 1b) and from $q_a q_s^2 + q_a^2 q_s$ (fig. 1c). We show below that in a typical case the contribution from diagram 1c dominates over that of diagram 1b by a factor ≈ 10–100. The leading contribution to damping via two-phonon emission comes from the term $q_a q_s^2$ (fig. 1a) and earlier treatments of this process are, therefore, unchanged [1–3].

For simplicity, we follow the formalism used by Persson and Ryberg [1]. Consider an atom of mass m adsorbed in on-top position on a substrate atom of mass M. We assume that $M \gg m$ and that a "high"-frequency mode occurs, involving mainly the adatom m vibrating relative to the metal atom M, with a resonance frequency ω_a higher than the cutoff frequency ω_m of the continuum band of low-frequency vibrations. We describe the interaction between the adatom and the nearest substrate atom by a Morse potential,

$$V(q)=D(\mathrm{e}^{-2\alpha q}-2\mathrm{e}^{-\alpha q}) \,. \tag{1}$$

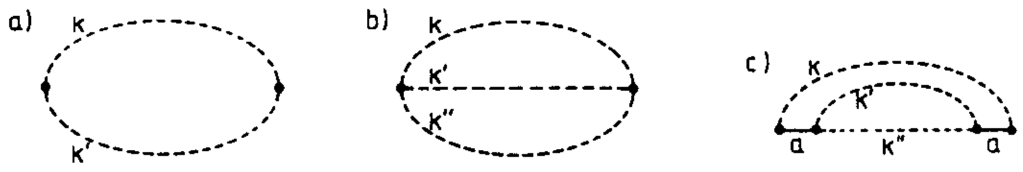

Fig. 1. Self-energy contributions to the propagator of the high-frequency mode "a". The solid lines denote the high-frequency propagator and the dashed lines are the propagators associated with the continuum band of phonons.

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Here, $q=u_a-u_s$, where u_a and u_s are the displacements from the equilibrium positions of the adatom and substrate atom, respectively, and $\alpha=m\omega_a^2/2D$ where D is the adsorption energy. We can represent the relative displacement coordinate,

$$q=q_a+q_s\,, \tag{2}$$

where, if $M \gg m$,

$$q_a=\left(\frac{1}{2m\omega_a}\right)^{1/2}(b_a+b_a^+),\quad q_s=\sum_\kappa\left(\frac{1}{2M\omega_\kappa N}\right)^{1/2}\frac{\omega_\kappa^2}{\omega_a^2-\omega_\kappa^2}\,\boldsymbol{e}_\kappa\cdot\boldsymbol{n}(b_\kappa+b_\kappa^+)\,, \tag{3}$$

and the subscript κ is a generalized quantum number specifying the low-frequency normal modes of the substrate in the presence of the adatom, and b_a and b_κ are annihilation operators for the high- and low-frequency modes, respectively. In (3), $\boldsymbol{n}$ is the surface normal, N is the number of substrate atoms and $\boldsymbol{e}_\kappa$ the polarization vector of mode κ. After expanding $V(q)$ in powers of q_a and q_s, and taking into account all quadratic terms in the harmonic part of the Hamiltonian, we obtain the model Hamiltonian,

$$H=H_0+H_1\,, \tag{4}$$

where

$$H_0=\omega_a b_a^+ b_a+\sum_\kappa \omega_\kappa b_\kappa^+ b_\kappa+6D\alpha^3Q_0^2 b_a^+ b_a q_s\,, \tag{5}$$

and $Q_0=(1/2m\omega_a)^{1/2}$. In comparison with previous treatments, we include in H_0 a contribution from the anharmonic term $\sim q_a^2 q_s$. The relevant terms in H_1 are

$$H_1=H_{12}+H_{13}\,, \tag{6}$$

$$H_{12}=-3D\alpha^3Q_0(b_a+b_a^+)q_s^2,\quad H_{13}=\tfrac{7}{3}D\alpha^4Q_0(b_a+b_a^+)q_s^3\,. \tag{7}$$

It has been assumed in the previous treatments that the main contribution to the linewidth, due to emission of three substrate phonons, is connected with the term H_{13}. We now note that the Hamiltonian H_0 can be diagonalized exactly using the following unitary transformation:

$$\tilde{H}_0=\mathrm{e}^{\mathrm{i}S}H_0\mathrm{e}^{-\mathrm{i}S}\,, \tag{8}$$

$$\mathrm{i}S=\sum_\kappa\frac{\tilde{\lambda}_\kappa}{\omega_\kappa}(b_\kappa^+-b_\kappa)b_a^+b_a,\quad \tilde{\lambda}_\kappa=6D\alpha^3Q_0^2\lambda_\kappa,\quad \lambda_\kappa=\left(\frac{1}{2M\omega_\kappa}\right)^{1/2}\frac{\omega_\kappa^2}{\omega_a^2-\omega_\kappa^2}\,\boldsymbol{e}_\kappa\cdot\boldsymbol{n}\,. \tag{9}$$

Via the identities,

$$\tilde{b}_\kappa=\mathrm{e}^{\mathrm{i}S}b_\kappa\mathrm{e}^{-\mathrm{i}S}=b_\kappa-\frac{\tilde{\lambda}_\kappa}{\omega_\kappa},\quad \tilde{b}_a=\mathrm{e}^{\mathrm{i}S}b_a\mathrm{e}^{-\mathrm{i}S}=\mathrm{e}^{-\mathrm{i}S_1}b_a,\quad \mathrm{i}S_1=\sum_\kappa\frac{\tilde{\lambda}_\kappa}{\omega_\kappa}(b_\kappa^+-b_\kappa)\,, \tag{10}$$

the transformed Hamiltonian H_{12} takes the form,

$$\tilde{H}_{12}=\mathrm{e}^{\mathrm{i}S}H_{12}\mathrm{e}^{-\mathrm{i}S}=-3D\alpha^3Q_0(b_a\mathrm{e}^{-\mathrm{i}S_1}+b_a^+\mathrm{e}^{\mathrm{i}S_1})q_s^2\,. \tag{11}$$

We have omitted the terms related to a constant shift ($q_s\to q_s+\Delta q$) of displacement coordinate q_s, which give a small contribution. The transformation (8) takes into account the shift in the equilibrium positions of the low-frequency oscillators during the transition of the high-frequency oscillator from its first excited state to the ground state. Owing to these shifts, the phonon states of the low-frequency modes, which are orthogonal before the transition, become non-orthogonal afterwards. This non-orthogonality leads to the possibility of multiphonon processes occurring already to second order in H_{12}. The shift in the equilibrium positions of the lattice atoms accompanying the relaxation of a high-frequency local vibration has been described earlier in connection with adiabatic perturbation theory [4]. The linewidth derived from the term H_{12} is determined by [5]

$$\Gamma=\frac{1}{1+n(\omega_a)}\int_{-\infty}^{\infty}\langle (H_{12}(t))_{01}(H_{12}(0))_{10}\rangle\,, \tag{12}$$

where $(H)_{01}=\langle 0|H|1\rangle$ is the matrix element of H between the vibrational ground state and the first excited state of the high-frequency mode and where

$$n(\omega_a)=\frac{1}{e^{\beta\omega_a}+1}\,,\quad H_{12}(t)=e^{iH_s t}H_{12}e^{-iH_s t},\quad H_s=\sum_\kappa \omega_\kappa b_\kappa^+ b_\kappa\,, \tag{13}$$

and $\beta=1/k_B T$ where T is the temperature and k_B the Boltzmann constant. The average in (12) is taken over the thermal equilibrium of the low-frequency modes,

$$\langle ...\rangle=\mathrm{Tr}(e^{-\beta H_s}...)/\mathrm{Tr}(e^{-\beta H_s})\,. \tag{14}$$

Substitution of H_{12} from (11) into (12) gives

$$\Gamma=\frac{9D^2\alpha^6Q_0^2}{1+n(\omega_a)}\int_{-\infty}^{\infty}\langle e^{iS_1(t)}q_s^2(t)q_s^2(0)e^{-iS_1(0)}\rangle\,, \tag{15}$$

where

$$iS_1(t)=\sum_\kappa\frac{\bar{\lambda}_\kappa}{\omega_\kappa}(b_\kappa^+e^{i\omega_\kappa t}-b_\kappa e^{-i\omega_\kappa t}),\quad q_s(t)=\sum_\kappa(b_\kappa e^{-i\omega_\kappa t}+b_\kappa^+e^{i\omega_\kappa t})\,. \tag{16}$$

The correlation function in (15) can be evaluated exactly, but the derivation is greatly simplified, without essential loss of accuracy, if we use the approximation,

$$\begin{aligned}&\langle e^{iS_1(t)}q_s^2(t)q_s^2(0)e^{-iS_1(0)}\rangle\approx\langle e^{iS_1(t)}e^{-iS_1(0)}\rangle\langle q_s^2(t)q_s^2(0)\rangle\\&\quad=2\langle e^{iS_1(t)}e^{-iS_1(0)}\rangle\{[\langle q_s(t)q_s(0)\rangle]^2+(\langle q_s^2\rangle)^2\}\,,\end{aligned} \tag{17}$$

and note that

$$\langle e^{iS_1(t)}e^{-iS_1(0)}\rangle=e^{-g(0)}e^{g(t)}\,, \tag{18}$$

$$g(t)=\sum_\kappa\frac{|\bar{\lambda}_\kappa|^2}{\omega_\kappa^2}\{[1+n(\omega_\kappa)]e^{-i\omega_\kappa t}+n(\omega_\kappa)e^{i\omega_\kappa t}\}\,, \tag{19}$$

$$\langle q_s(t)q_s(0)\rangle=\sum_\kappa|\bar{\lambda}_\kappa|^2\{[1+n(\omega_\kappa)]e^{-i\omega_\kappa t}+n(\omega_\kappa)e^{i\omega_\kappa t}\}\,. \tag{20}$$

Expanding (18) in a power series and taking into account only phonon emission processes, one finds that (15) gives

$$\Gamma=\frac{9\pi}{16}\frac{\omega_a}{D}\left(\frac{m}{M}\right)^2\frac{\omega_a K}{1+n(\omega_a)}\,, \tag{21}$$

where

$$\begin{aligned}K=&\sum_{n=0}^{\infty}\left(\frac{9m\omega_a}{16MD}\right)^n\frac{1}{n!}\int d\omega_1\,...d\omega_{n+1}\,\frac{\omega_a^{3n+3}}{\omega_1^3...\omega_n^3\omega_{n+1}(\omega_a-\omega_1-...-\omega_{n+1})}\\&\times\rho(\omega_1)\,..\rho(\omega_a-\omega_1-...-\omega_{n+1})\\&\times[1+n(\omega_1)]\,...[1+n(\omega_a-\omega_1-...-\omega_{n+1})]\times P(\omega_1)\,...P(\omega_a-\omega_1-...-\omega_{n+1})\,.\end{aligned} \tag{22}$$

Here, $P(\omega)=[\omega^2/(\omega_a^2-\omega^2)]^2$ is the reduction factor which was first derived by Persson and Ryberg [1] for

-48-

$m \ll M$ and later by Langreth et al. [6] for a more general case. The density of states is given by

$$\rho(\omega) = \sum_{\kappa} |e_\kappa \cdot n|^2 \delta(\omega - \omega_\kappa) . \tag{23}$$

In formula (22), emission of $n+2$ phonons corresponds to the nth term in the sum and, in particular, the three-phonon contribution is determined by the $n=1$ term, corresponding to the process indicated in fig. 1c. Comparing this contribution to the linewidth with the contribution from fig. 1b, as obtained by Persson and Ryberg for the special case when $\rho(\omega)$ has a sharp peak at the frequency ω_0 carrying most of the spectral weight, we obtain

$$\Gamma_3/\Gamma_3^0 \sim (\omega_a/\omega_0)^2 , \tag{24}$$

where Γ_3 and Γ_3^0 are the linewidths due to the three-phonon decay from processes 1c and 1b, respectively. For the Pt–CO stretch vibration for CO on Pt(111), where $\omega_a = 460$ cm^{-1} and $\omega_0 = 70$ cm^{-1}, this ratio becomes ≈ 40. Although this result does not change the conclusion of ref. [1], i.e. three-phonon processes still give a negligible contribution to the observed linewidth, it will be important for other systems, such as adsorbate vibrations on insulators or semiconductors. In general, the contribution from the term H_{13} is $\sim (\omega_a/\omega_0)^{2(n-2)}$ times greater than the contribution from the term $q_a q_s^n$, taken to lowest order of perturbation theory.

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VIBRATIONAL LINESHAPES OF ADSORBED MOLECULES

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The vibrational lineshapes of adsorbed molecules are treated theoretically. It is shown that for vibration parallel to the surface the presence of the electron–hole damping mechanism necessarily produces an asymmetric lineshape just as in the case of vibration normal to the surface. In the case of dephasing of an adsorbate vibration due to elastic scattering of electrons the linewidth has a small T dependence. The exchange model of vibrational phase relaxation with a quartic and cubic anharmonism is studied by a new method. The vibrational line profile is calculated exactly.

1. Introduction

Considerable recent work has been aimed on the interpretation of adsorbate linewidth and lineshapes on metal surfaces with the goal of extracting information on adsorbate–metal interactions from such studies [1–4]. In particular, the origin of the observed linewidth continues to be an open question, requiring more quantitative theoretical work, new experimental data, and the examination of all relevant mechanisms. An excellent review of the theory of line-broadening has been given by Gadzuk and Luntz [1]. Recent experimental determinations of the line-broadening mechanism are reviewed by Tobin [2]. The processes can be broadly classified as lifetime broadening, dephasing, and inhomogeneous broadening.

On metallic substrates, the electron–hole pair provides an important channel for vibrational decay. As it was pointed out by Langreth [5] the inescapable consequence of this electron–hole decay mechanism is that the lineshape is an asymmetric Lorentzian tailing on either side of the resonance frequency depending on certain parameters pertinent to the system considered. The results of Langreth's work were used by Chabal [6] for the interpretation of the experimental data of the overtone infrared adsorption of the wagging mode of H on W(100) at saturation coverage. However, Langreth considered the fundamental mode of a vibration polarized normal to the surface while the wagging mode is polarized parallel to the surface. Thus without further investigations it is not clear why the results obtained for the mode polarized normal to the surface are valid for the mode polarized parallel to the surface.

The dephasing rate of an adsorbate vibration due to elastic electron–hole pair scattering has been considered by Moravitz [7] and Zhdanov [8]. They used an identical approach but obtained different results. More important is that they neglected the more important processes due to elastic electron scattering which occur in the fourth order perturbation theory.

In a recent series of papers, Persson et al. [9–11] have presented theoretical calculations of the vibrational lineshape based on the exchange model for phase relaxation. This model was proposed by Harris and co-workers [12] to explain the vibrational lineshapes of high-frequency modes of polyatomic impurities in condensed phases. The physical picture used to describe vibrational dephasing by the exchange mechanism for an adsorbed molecule can be described as follows. The high-frequency mode interacts with low-frequency local modes such as frustrated translations or frustrated rotations of the adsorbate. The latter are coupled to the lattice phonons. The anharmonic coupling between the high-frequency mode and the low-frequency fluctuating mode is the source of the former's dephasing. The simplest model of this process is described by the Hamiltonian

$$H = H_a + H_b + H_s + H_{ab} + H_{sb}, \tag{1}$$

$$H_a = \omega_a a^+ a, \tag{2}$$

$$H_b = \omega_b b^+ b, \tag{3}$$

$$H_s = \sum_k \omega_k b_k^+ b_k, \tag{4}$$

$$H_{bs} = \sum_k V_k b^+ b_k + \text{h.c.}, \tag{5}$$

where a is the annihilation operator for the high-frequency mode A (of frequency ω_a) under study, b is the annihilation operator for the low-frequency local mode B (of frequency ω_b), b_k is the annihilation operator for the thermal bath (of frequency ω_k), V_k is the coupling constant for the interaction of the lattice mode with the low-frequency mode B. The Hamiltonian H_{ab} describes the anharmonic coupling between modes A and B. In symmetry cases such as bridge-bonded CO stretch coupled with a frustrated rotation or translation on Ni(111) [9] the most important contribution comes from the quartic term $u_a^2 u_b^2$ in the anharmonic part of the interaction Hamiltonian H_{ab}, where u_a and u_b are the vibrational coordinates for the modes A and B respectively. In these cases

$$H_{ab} = \delta\omega a^+ a b^+ b. \tag{6}$$

The exchange model with quartic anharmonism was considered by Persson et al. [9–11]. The vibrational line profile was obtained analytically in various limiting cases such as high temperature and large friction. In the general case the vibration lineshape was calculated numerically.

In less symmetrical situations cubic terms such as $a^+a(b^++b)$, $aa(b^++b)$ and $a^+a^+(b^++b)$ will also appear. As it was shown by Langreth et al. [13] non-diagonal terms $aa(b^++b)$, $a^+a^+(b^++b)$ make pure dephasing contributions when one reaches fourth-order perturbation theory. Nevertheless, its fourth-order contribution to dephasing is formally of the same size as the leading contribution of the quartic term. A cubic term not only gives a dephasing contribution to the central peak at frequency ω_a, but also produces satellites at $\omega_a \pm \omega_b$, $\omega_a \pm 2\omega_b$, ... due to a diagonal term $a^+a(b^++b)$. The lineshape of the satellites was calculated approximately by Langreth et al. [13].

The article proceeds as follows. In section 2 the lineshapes for isolated vibrational modes polarized parallel and normal to the surface of an atom adsorbed on a metallic surface in the presence of electron-hole damping mechanism are calculated. For a vibration normal to the surface we take into account the diagram which was not considered by Langreth [3,5]. With this diagram the small temperature dependence of the lineshape can be taken into account. In section 3 dephasing due to elastic electron scattering is considered. All diagrams up to the fourth order perturbation theory are included. In section 4 the exchange model with quartic and cubic anharmonism are considered. For cubic anharmonism only the diagonal cubic term $a^+a(b^++b)$ is taken into account. For this exchange model the vibrational line profile is calculated exactly.

2. Asymmetric lineshape due to the electron–hole pair loss mechanism

2.1. Vibration normal to the surface

We consider a chemisorbed molecule on a metal surface within the Anderson–Newns model supplemented with a lattice distortion. The model Hamiltonian of the present case is described by

$$H = H_{\mathrm{el}} + H_{\mathrm{ph}} + H_{\mathrm{el-ph}}, \tag{7}$$

$$H_{\mathrm{el}} = \epsilon_a n_a + \sum_k \epsilon_k n_k + \sum_k V_{ak} c_a^+ c_k + \mathrm{h.c.}, \tag{8}$$

$$H_{\mathrm{ph}} = \omega_a b^+ b, \tag{9}$$

$$H_{\mathrm{el-ph}} = \epsilon_a' n_a u_a, \tag{10}$$

where $n_a = c_a^+ c_a$, $n_k = c_k^+ c_k$, and $c_a^+(c_a)$ and $c_k^+(c_k)$ are the fermion creation (annihilation) operators of electrons in the molecule and the metal, respectively. $u_a = Q_0(b^+ + b)$, $b^+(b)$ is the creation (annihilation) operator of localized phonon, $Q_0 = (2m\omega_a)^{-1/2}$, m is the effective mass and ω_a is the vibrational frequency, $\epsilon_a' = d\epsilon_a/du_a$. The coupling to the infrared electric field is described by a perturbation

$$H_I = \hat{\mu}\left(E_0\, e^{i\omega t} + E_0^*\, e^{-i\omega t}\right). \tag{11}$$

We note that at IR frequencies screening by the metal electrons occurs in such a way that no component of the electric field parallel to the surface can arise at the interface. If we pick our origin on the image plane of the substrate which we assume is the mean position of all induced substrate charge then

$$\hat{\mu} = \mu_0 n_a + (\mu_e n_a + \mu_i)(b^+ + b), \tag{12}$$

where

$$\mu_0 = \int d^3x\, e\boldsymbol{n}\cdot\boldsymbol{x}\,|\varphi_a(\boldsymbol{x})|^2, \tag{13}$$

$\boldsymbol{n}$ is the unit vector normal to the surface, $\varphi_a(\boldsymbol{x})$ is the orbital wavefunction for the adsorbate localized orbital, μ_i is the ionic contribution to the dynamic dipole moment, $\mu_e n_a$ is the operator corresponding to an electronic contribution to the dynamic dipole moment.

According to the linear response theory [14] the polarizability is given by

$$\alpha(\omega) = \langle\langle\hat{\mu}, \hat{\mu}\rangle\rangle_{\omega+i\delta} = -i\int_0^\infty e^{i\omega t}\langle[\hat{\mu}(t)\hat{\mu}(0)]\rangle\, dt, \tag{14}$$

where $\langle\cdots\rangle$ is the thermal average. It is actually most convienient from the point of view of doing perturbation theory to work with the temperature Green's function [15]. The retarded Green's function $\langle\langle\hat{\mu}, \hat{\mu}\rangle\rangle_{\omega+i\delta}$ can be determined by analytic continuation of the temperature Green's function from the imaginary axis to the real axis [15]. The quantity $\langle\langle\hat{\mu}, \hat{\mu}\rangle\rangle$ can be expressed as

$$\begin{aligned}\langle\langle\hat{\mu}, \hat{\mu}\rangle\rangle = {}& \mu_0^2\langle\langle n_a, n_a\rangle\rangle + \mu_i^2\langle\langle\varphi, \varphi\rangle\rangle + \mu_e^2\langle\langle n_a\varphi, n_a\varphi\rangle\rangle \\ & + \mu_0\langle\langle n_a, n_a\varphi\rangle\rangle\mu_e + \mu_e\langle\langle n_a\varphi, n_a\rangle\rangle\mu_0 \\ & + \mu_0\langle\langle n_a, \varphi\rangle\rangle\mu_i + \mu_i\langle\langle\varphi, n_a\rangle\rangle\mu_0 \\ & + \mu_e\langle\langle n_a\varphi, \varphi\rangle\rangle\mu_i + \mu_i\langle\langle\varphi, n_a\varphi\rangle\rangle\mu_e,\end{aligned} \tag{15}$$

where $\varphi = b^+ + b$. Diagrammatic representations of the various Green's function which contributes to $\langle\langle\hat{\mu}, \hat{\mu}\rangle\rangle$ in leading order in $\delta\epsilon_1 = \epsilon_a' Q_0$ are shown in fig. 1. These diagrams can be evaluated in an exactly analogous manner as in Langreth's paper [3]. Analytical expressions for this Green's function are given by

$$\langle\langle n_a, n_a\rangle\rangle = \Pi_0 + (\delta\epsilon_1)^2\Pi_0 D\Pi_0, \tag{16}$$

$$D = \langle\langle\varphi, \varphi\rangle\rangle = \frac{2\omega_a}{\omega^2 - \omega_a^2 - 2\omega_a(\delta\epsilon_1)^2\Pi_0}, \tag{17}$$

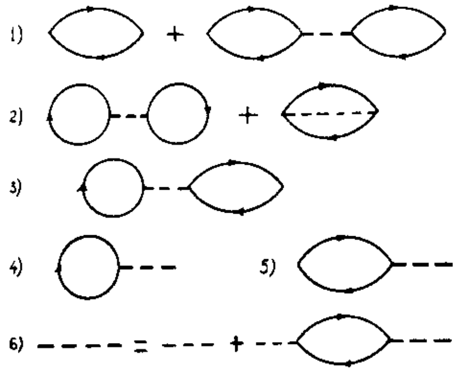

Fig. 1. Diagrammatic representation of (1) $\langle\langle n_a, n_a\rangle\rangle$; (2) $\langle\langle n_a\varphi, n_a\varphi\rangle\rangle$; (3) $\langle\langle n_a\varphi, n_a\rangle\rangle$; (4) $\langle\langle n_a\varphi, \varphi\rangle\rangle$; (5) $\langle\langle n_a, \varphi\rangle\rangle$; (6) $\langle\langle \varphi, \varphi\rangle\rangle$ for vibration normal to the surface. The solid line represents the electron Green's functions while the dashed line represents the phonon Green's function.

$$\langle\langle n_a\varphi, n_a\varphi\rangle\rangle = \langle n_a\rangle^2 D + I, \tag{18}$$

$$\langle\langle n_a, n_a\varphi\rangle\rangle = \langle\langle n_a\varphi, n_a\rangle\rangle = \delta\epsilon_1 \Pi_0 D \langle n_a\rangle, \tag{19}$$

$$\langle\langle n_a, \varphi\rangle\rangle = \langle\langle \varphi, n_a\rangle\rangle = \delta\epsilon_1 \Pi_0 D, \tag{20}$$

$$\langle\langle n_a\varphi, \varphi\rangle\rangle = \langle\langle \varphi, n_a\varphi\rangle\rangle = \langle n_a\rangle D, \tag{21}$$

where at $\Delta \gg \omega_a$ and $|\omega - \omega_a| < T$ (Δ is the electron half width, T is the temperature)

$$\Pi_0 = -\rho_a(0)\left[1 + i\pi\rho_a(0)\omega\right], \tag{22}$$

$$\rho_a(\epsilon) = \frac{1}{\pi}\frac{\Delta}{(\epsilon - \epsilon_a)^2 + \Delta^2}, \tag{23}$$

$$\operatorname{Im} I = -\pi\rho_a^2(0)T. \tag{24}$$

Note that in comparison with Langreth's work [3] we take into account the contribution I. Then combining the results (16)–(21) in eq. (15) gives

$$\langle\langle \hat\mu, \hat\mu\rangle\rangle = \mu_e^2\Pi_0 + \mu^2 D + \mu_e^2 I,$$

where

$$\mu_1 = \operatorname{Re}\mu = \mu_i + \mu_0\langle n_a\rangle + \mu_0\delta\epsilon_1 \operatorname{Re}\Pi_0, \tag{25}$$

$$\mu_2 = \operatorname{Im}\mu = \mu_0\delta\epsilon_1 \operatorname{Im}\Pi_0. \tag{26}$$

The lineshape is given by:

$$L(\omega) = -\operatorname{Im}\alpha(\omega) = L_r(\omega) + L_b, \tag{27}$$

$$L_r(\omega) = \frac{2\omega_0\mu_1^2}{\omega\gamma}\frac{(1 - xy)^2}{1 + x^2}, \tag{28}$$

$$L_b = \mu_0^2 \pi \rho_a^2(0) T, \tag{29}$$

where $y = \omega\tau$, $x = (\omega^2 - \omega_a^2)/\omega\gamma$,

$$\tau = \pi(\mu_0/\mu_1)\delta\epsilon_1\rho_a^2(0), \tag{30}$$

$$\gamma = 2\pi\omega_a(\delta\epsilon_1\rho_a(0))^2. \tag{31}$$

The resonance part $L_r(\omega)$ was firstly calculated by Langreth [5]. It has a characteristic asymmetric shape. L_b is a T dependent background which was neglected by Langreth [3,5]. At the resonance frequency

$$\frac{L_r^{\max}}{L_b} \approx \left(\frac{r_0}{Q_0}\right)^2 \frac{\Delta^2}{\omega_a T},$$

where r_0 is the distance between the centre of gravity of the adsorbate charge and the image plane. For hydrogen vibration on a tungsten surface $(r_0/Q_0)^2 \approx 10$, $\Delta \approx 1$ eV, $\omega_a \approx 0.1$ eV. At room temperature $L_r^{\max}/L_b \approx 10^4$ thus the background intensity is negligible with respect to the resonance intensity. However at $\gamma \ll |\omega - \omega_a| < T$

$$\frac{L_r}{L_b} \sim \left(\frac{r_0}{Q_0}\right)^2 \frac{\omega}{T}.$$

Thus at $T \approx \omega$ the background intensity would be significant. For the C–O stretching vibration mode on Cu(100) $(Q_0/r_0)^2 \approx 10^{-4}$ thus the background intensity is always small with respect to the resonance one.

2.2. Vibration parallel to the surface

For vibration parallel to the surface for symmetry site of adsorption $\epsilon_a(-u_a) = \epsilon_a(u_a)$ and $\Delta(-u_a) = \Delta(u_a)$ thus $\epsilon_a' = \Delta' = 0$ but $V_{ak}' \neq 0$. The Hamiltonian again can be written in the form (7) where H_{el} and H_{ph} are given by (8) and (9) but

$$H_{el-ph} = \delta\epsilon_2/2(b^+ + b)^2 + u_a \sum_k V_{ak}' c_a^+ c_k + \text{h.c.}, \tag{32}$$

$$\delta\epsilon_2 = \epsilon_a'' Q_0^2, \quad \epsilon_a'' = \mathrm{d}^2\epsilon_a/\mathrm{d}u_a^2, \quad V_{ak}' = \mathrm{d}V_{ak}/\mathrm{d}u_a.$$

The coupling to the infrared electric field is described by

$$H_1 = \mu_0 n_a(E_0\,\mathrm{e}^{i\omega t} + E_0^*\,\mathrm{e}^{-i\omega t}), \tag{33}$$

because μ_i and μ_e are equal to zero from symmetry reasons. Note that for vibration parallel to the surface we take into account the term V_{ak}' in the Hamiltonian (32). For vibration normal to the surface this term does not change qualitatively the results obtained above. However as it will be shown later this term is important for vibration parallel to the surface.

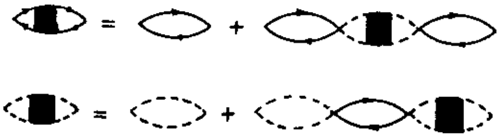

Fig. 2. Diagrammatic representation of $\langle\langle n_a, n_a\rangle\rangle$ for vibration parallel to the surface. The solid and dashed lines have the same meaning as in fig. 1.

The lineshape is determined by

$$L(\omega) = -\operatorname{Im}\langle\langle n_a, n_a\rangle\rangle. \tag{34}$$

As for vibration normal to the surface the Green's function $\langle\langle n_a, n_a\rangle\rangle$ can be evaluated using a diagrammatic technique. Neglecting the small temperature effect we can use the diagrammatic technique for $T = 0$ K. In this technique the imaginary parts of the Green's functions for $\omega > 0$ are the same for the appropriate transform of the time ordered functions as they are for the retarded commutators and this allows us to deal with the former, since we can take $\omega > 0$ without any real loss in generality. The Green's function $G = -i\langle \hat{T} n_a(t) n_a(0)\rangle$, where $\hat{T}$ is the time-ordering operator, obeys the Dyson equations which are shown in fig. 2. Analytical expression of these equations have the form

$$G = \Pi_0 + \Pi_0 M \Pi_0, \quad M = M_0 + M_0 \Pi_0 M, \tag{35}$$

where Π_0 is determined by (22),

$$M_0 = \mathrm{i}\frac{(\delta\epsilon_2)^2}{2}\int_{-\infty}^{\infty}\frac{\mathrm{d}\omega'}{2\pi}D(\omega')D(\omega-\omega'), \tag{36}$$

$$D(\omega) = \frac{2\omega_a}{\omega^2 - \omega_a^2 + \mathrm{i}\,|\omega|\,\gamma_1}, \tag{37}$$

$$\gamma_1 = \frac{2}{\pi m}\sin^2\delta(0)\frac{W(0)}{\Delta}, \tag{38}$$

$$\delta(\epsilon) = \mathrm{tg}^{-1}\frac{\Delta}{\epsilon_a - \epsilon}, \tag{39}$$

$$W(\epsilon) = \pi\sum_k |V'_{ak}|^2\delta(\epsilon - \epsilon_k). \tag{40}$$

Evaluation of the integral in formula (36) leads to the result

$$M_0(\omega) = \frac{2\Omega}{\omega^2 - \Omega^2 + \mathrm{i}\,|\omega|\,\gamma_1}, \tag{41}$$

$$\Omega = 2\omega_a.$$

From eq. (35) we obtain

$$M(\omega)=\frac{(\delta\epsilon_2)^2}{2}\frac{2\Omega}{\omega^2-\Omega^2+\mathrm{i}\,|\,\omega\,|\,\gamma}, \tag{42}$$

$$\gamma=\gamma_1+\gamma_2, \tag{43}$$

$$\gamma_2=2\pi\omega_a(\delta\epsilon_2\rho_a(0))^2, \tag{44}$$

Usually the condition $\gamma_1 \gg \gamma_2$ is valid then $\gamma \simeq \gamma_1$. The damping constants γ_1 and γ_2 have different isotope dependences. Since $(\delta\epsilon_1)^2 \sim m^{-1/2}$, $(\delta\epsilon_2)^2 \sim m^{-1}$, then $\gamma_2 \sim m^{-1}$ and $\gamma_2 \sim m^{-3/2}$. For $\gamma_1 \gg \gamma_2$ the lineshape is determined by (27) where as for vibration normal to the surface the resonance part is determined by (28) with $\omega_a \to \Omega = 2\omega_a$,

$$\tau=\pi\rho_a(0), \tag{45}$$

$$\mu_1=\mu_0(\delta\epsilon_2/\sqrt{2})\rho_a(0), \tag{46}$$

$$\gamma \simeq \gamma_1. \tag{47}$$

The background intensity is determined by

$$L_b(\omega)=\mu_0^2\pi\rho_a^2(0)\,\omega. \tag{48}$$

Thus for a vibration parallel to the surface the resonance part $L_r(\omega)$ has a peak at the overtone frequency $\omega=\Omega=2\omega_a$. The characteristic lineshape predicted by formula (28) has been observed by Chabal [6] for the overtone of the wagging mode of H on W(100). Since $L_r(\omega) \sim (\delta\epsilon_2)^2$ which in general is small the intensity of the overtone peak would be weak. The unusual strength of the overtone of the wagging mode of H on W(100) is due to a strong coupling of the wag mode to surface electronic states located at the Fermi level [6]. For $|\omega-\Omega| > \gamma$ for parallel vibration $L_r/L_b \sim \gamma_2/\gamma_1 \ll 1$ thus outside the resonance region the background part would be stronger then the resonance one. Since for normal (parallel) vibration $\mu_1^2 \sim m^{-1/2}$ (m^{-1}) and in both cases $\gamma \sim m^{-1}$ then at the resonance frequency $L_0^{\max} \sim \mu_1^2/\gamma \sim m^{1/2}$ for normal vibration and does not depend on the mass for parallel vibration.

3. Dephasing due to elastic electron scattering

Let us again consider Hamiltonian (7), where H_{el} and H_{ph} are given by (8) and (9),

$$H_{el-ph}=(\epsilon'_a u_a+\epsilon''_a/2u_a^2+\cdots)n_a. \tag{49}$$

The vibrational linewidth is determined by the phonon self-energy $\Pi(\omega)$

$$\Gamma=-\mathrm{Im}\,\Pi_R(\omega+\mathrm{i}\delta). \tag{50}$$

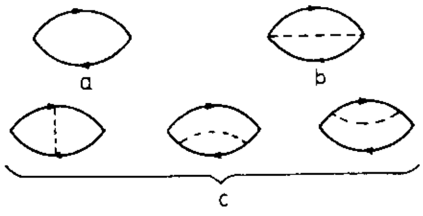

Fig. 3. Second- and fourth-order perturbation theory diagrams for the phonon self-energy $\Pi(i\omega_n)$. The solid and dashed lines have the same meaning as in fig. 1.

Instead of the retarded Green's function (50) we can again consider the temperature Green's function $\Pi(i\omega_n)$ for which there is a diagrammatic technique. The Feynman diagrams which give rise to the phonon self-energy $\Pi(i\omega_n)$ up to the fourth-order perturbation theory are shown in fig. 3. Diagram "a" can give damping in second-order processes by creating electron–hole pair excitation. The diagrams "b" and "c" can give dephasing in second- and fourth-order processes, respectively, by elastic electron scattering. These diagrams were evaluated by Volokitin [16]. The contributions to Γ from the self-energy diagrams Π_a, Π_b and Π_c are given by

$$\Gamma_a = \Gamma_a(0) + \frac{\pi^2}{6} \frac{\partial^2 \Gamma_a}{\partial \epsilon^2}\bigg|_{\epsilon=0} T^2, \tag{51}$$

$$\Gamma_a(\epsilon) = 2\pi\omega_a(\rho_a(\epsilon)\delta\epsilon_1)^2, \tag{52}$$

$$\Gamma_b = 2\pi(\rho_a(0)\delta\epsilon_2)^2 T, \tag{53}$$

$$\Gamma_c = 8\pi(\delta\epsilon_1)^4 (G_a'(0))^2 \rho_a^2(0) T, \tag{54}$$

$$G_a'(\epsilon) = \frac{\epsilon - \epsilon_a}{(\epsilon - \epsilon_a)^2 + \Delta^2}. \tag{55}$$

Let us make estimations of the various contributions. Since $\partial^2\Gamma_a/\partial\epsilon^2 \sim \Gamma_a(0)/\Delta$, $\delta\epsilon_2 \sim \delta\epsilon_1 Q_0/d$, where d is the distance over which the adsorbate level position changes significantly, then for $|\epsilon_a| \approx \Delta$ we obtain

$$\delta\Gamma_a/\Gamma_a \sim (T/\Delta)^2, \quad \delta\Gamma_a = \Gamma_a - \Gamma_a(0),$$

$$\Gamma_b/\Gamma_a \sim (Q_0/d)^2 T/\omega_0,$$

$$\Gamma_c/\Gamma_a \sim 4\pi^2(\delta\epsilon_1/\Delta)^2(T/\omega_a).$$

For typical chemisorption systems $Q_0/d \approx 10^{-1}$–10^{-2}, $\delta\epsilon_1/\Delta \approx 10^{-1}$–$10^{-2}$, $\omega_a/\Delta \approx 10^{-1}$. Then for the temperature region $T/\omega_a \approx 1$–10^{-1} we obtain

$$\delta\Gamma_a/\Gamma_a \approx 10^{-2}\text{–}10^{-6},$$

$$\Gamma_b/\Gamma_a \approx 10^{-2}\text{–}10^{-5},$$

$$\Gamma_c/\Gamma_a \approx 10^{-1}\text{–}10^{-4}.$$

Thus from our estimations one can conclude that in many cases the temperature contribution to the linewidth due to electron dephasing processes is negligible which is in sharp contradiction with the results obtained by Moravitz [7]. However, it may be shown that the ratio of the Moravitz's dephasing contribution due to elastic electron–hole pair scattering to Γ_c is of the order $(T/\Delta)^2 \ll 1$. The large contribution obtained by Moravitz is related with the nonrealistic estimation for the adsorbate density of state $\rho_a(0)$. Contrarily to our calculation, Moravitz as well as Zhdanov do not take into account the main contributions to the temperature dependence of the linewidth due to elastic scattering of electrons. The temperature dependent contribution to the linewidth due to electron dephasing processes may be significant only at high temperature and strong electron–phonon interaction when $T \approx \omega_a$, $\delta\epsilon_1 \rho_a(0) \approx 1$. For example, for a hydrogen vibration $\delta\epsilon_1$ may be of the order 0.1–1 eV. In this case the temperature dependent contribution to the linewidth due to electron dephasing processes may be significant when there is an electron resonance of the adsorbate near the Fermi level with a half width $\Delta \approx 0.1$–1 eV.

4. Exchange model

4.1. Quartic anharmonism

The exchange model with quartic anharmonism is determined by formulas (1)–(6). The lineshape may be written as

$$L(\omega) = \mathrm{Re}\int_0^{\omega} \mathrm{e}^{\mathrm{i}(\omega-\omega_a)t} S(t)\, \mathrm{d}t,$$

where $S(t)$ is the response function which for the high frequency vibrational mode A ($\omega_a \gg T$) can be written in the form

$$\begin{aligned} S(t) &= \mathrm{e}^{\mathrm{i}\omega_a t}\langle [a(t)a^+(0)] \rangle \approx \mathrm{e}^{\mathrm{i}\omega_a t}\langle a(t)a^+(0)\rangle_0 \\ &= \mathrm{e}^{\mathrm{i}\omega_a t}\langle \mathrm{e}^{\mathrm{i}H_0 t}\, \mathrm{e}^{-\mathrm{i}H_1 t}\rangle_0 = \langle \hat{S}(t)\rangle_0 . \end{aligned}$$

$$\hat{S}(t) = \hat{T}\exp\left[-\mathrm{i}\delta\omega\int_0^t b^+(\tau)b(\tau)\, \mathrm{d}\tau\right],$$

$$\langle \cdots \rangle = \mathrm{Sp}(\mathrm{e}^{-\beta H}\cdots)/\mathrm{Sp}(\mathrm{e}^{-\beta H}),$$

$$\langle \cdots \rangle_0 = \mathrm{Sp}(\mathrm{e}^{-\beta H_0}\cdots)/\mathrm{Sp}(\mathrm{e}^{-\beta H_0}), \tag{56}$$

$\beta = T^{-1}$, $H_i = \langle i | H | i \rangle$, $| i \rangle$ is the phonon state for the high-frequency mode A, $a^+ a | i \rangle = i | i \rangle$, $i = 0, 1$. We are thus interested in the transient response of substrate phonons to the abrupt change of frequency ω_b (from ω_b to $\omega_b + \delta\omega$).

The linked cluster theorem tells us that

$$S(t) = \mathrm{e}^{F(t)}, \tag{57}$$

where $F(t)$ is the contribution of all single closed loops. Let us introduce a new variable $\delta\omega \to \lambda$. Then it may be shown that $F(t)$ obeys the equation

$$\frac{\mathrm{d}F(t)}{\mathrm{d}\lambda} = \int_0^t G(\tau - 0, \tau, t)\, \mathrm{d}\tau, \tag{58}$$

where

$$G(\tau, \tau', t) = -\mathrm{i}\frac{\langle \hat{T} b(\tau) b^{+}(\tau') \hat{S}(t)\rangle_0}{\langle \hat{S}(t)\rangle_0} \tag{59}$$

obeys the Dyson equation

$$G(\tau, \tau', t) = G_0(\tau - \tau') + \lambda \int_0^t G_0(\tau - \tau'') G(\tau'', \tau', t)\, \mathrm{d}\tau''. \tag{60}$$

The integral equation (60) was also obtained by Nozieres and Dominicis in their famous work on the X-ray absorption and emission of metals [17]. The difference between these cases is in the kernel of the integral equation. In the boson case at $\omega_\mathrm{b} \gg \Gamma_\mathrm{b}$, where $\Gamma_\mathrm{b} = \pi \Sigma_k | V_k |^2 \delta(\omega - \omega_k)$ is the half-width of the low-frequency mode B, the phonon Green's function $G_0(\tau)$ can be written in the form

$$\begin{aligned} G_0(\tau) &= -\mathrm{i}\langle \hat{T} b(\tau) b^{+}(0)\rangle_0 \\ &= -\mathrm{i}\, \mathrm{e}^{-\mathrm{i}\omega_\mathrm{b}\tau - \Gamma_\mathrm{b}|\tau|}\left[(1 + n_\mathrm{b})\theta(\tau) + n_\mathrm{b}\theta(-\tau)\right], \end{aligned} \tag{61}$$

$$\theta(\tau) = \begin{cases} 1, & \tau > 0, \\ 0, & \tau < 0, \end{cases}$$

where $n_\mathrm{b} = \langle b^{+} b\rangle_0 = [\exp(\beta\omega_\mathrm{b}) - 1]^{-1}$. In this case it may be shown that the integral equation (60) is equivalent to the following differential equation

$$\begin{aligned} &\frac{\mathrm{d}^2}{\mathrm{d}\tau^2}\tilde{G} + \mathrm{i}\lambda(\tau)\frac{\mathrm{d}\tilde{G}}{\mathrm{d}\tau} - \left[\Gamma_\mathrm{b}^2 + \mathrm{i}\lambda(\tau)\Gamma_\mathrm{b}(2n_\mathrm{b} + 1)\right]\tilde{G} \\ &\quad = -\mathrm{i}\frac{\mathrm{d}}{\mathrm{d}\tau}\delta(\tau - \tau') + \mathrm{i}\Gamma_\mathrm{b}(2n_\mathrm{b} + 1)\delta(\tau - \tau') \\ &\qquad -\mathrm{i}\lambda\left[\tilde{G}(0, \tau', t)\delta(\tau) - \tilde{G}(t, \tau', t)\delta(\tau - t)\right], \end{aligned} \tag{62}$$

where

$$\tilde{G}(\tau, \tau', t) = \exp\left[\mathrm{i}\omega_\mathrm{b}(\tau - \tau')\right] G(\tau, \tau', t), \quad \lambda(\tau) = \lambda\left[\theta(\tau) - \theta(\tau - t)\right].$$

The solution of the differential equation (62) has the form ($0 < \tau' < t$)

$$\begin{aligned}\tilde{G}(\tau, \tau', t) &= \mathrm{i}\frac{\mathrm{d}\omega_+}{\mathrm{d}\lambda}\mathrm{e}^{-\mathrm{i}\omega_+(\tau-\tau')}\theta(\tau'-\tau) - \mathrm{i}\frac{\mathrm{d}\omega_-}{\mathrm{d}\lambda}\mathrm{e}^{-\mathrm{i}\omega_-(\tau-\tau')}\theta(\tau-\tau') \\ &\quad + B\,\mathrm{e}^{-\mathrm{i}\omega_-\tau} + C\,\mathrm{e}^{-\mathrm{i}\omega_+(t-\tau)}, \quad \text{for } 0<\tau<t \\ &= A\,\mathrm{e}^{\Gamma_\mathrm{b}\tau}, \quad \text{for } \tau<0 \\ &= B\,\mathrm{e}^{-\Gamma_\mathrm{b}(\tau-t)}, \quad \text{for } \tau>t, \end{aligned} \tag{63}$$

where

$$\omega_\pm = \frac{\lambda}{2} \mp \left[\left(\frac{\lambda}{2}\right)^2 - \Gamma_\mathrm{b}^2 - \mathrm{i}\lambda\Gamma_\mathrm{b}(2n_\mathrm{b}+1)\right]^{1/2}, \tag{64}$$

$\mathrm{Im}\,\omega_+ > 0$, $\mathrm{Im}\,\omega_- < 0$.

The coefficients A, B, C and D are determined from the boundary conditions at $\tau = 0, t$

$$\begin{aligned} &\tilde{G}(-0, \tau, t) = \tilde{G}(+0, \tau', t), \quad \tilde{G}(t-0, \tau', t) = \tilde{G}(t+0, \tau', t), \\ &\frac{\mathrm{d}}{\mathrm{d}\tau}\tilde{G}(\tau, \tau', t)\Big|_{\tau=+0} - \frac{\mathrm{d}}{\mathrm{d}\tau}\tilde{G}(\tau, \tau', t)\Big|_{\tau=-0} = -\mathrm{i}\lambda\tilde{G}(0, \tau', t), \\ &\frac{\mathrm{d}}{\mathrm{d}\tau}\tilde{G}(\tau, \tau', t)\Big|_{\tau=t+0} - \frac{\mathrm{d}}{\mathrm{d}\tau}\tilde{G}(\tau, \tau', t)\Big|_{\tau=t-0} = \mathrm{i}\lambda\tilde{G}(t, \tau', t). \end{aligned} \tag{65}$$

From the boundary conditions we obtain

$$B = -\mathrm{i}\left(-Q\,\mathrm{e}^{\mathrm{i}\omega_+\tau'}\frac{\mathrm{d}\omega_+}{\mathrm{d}\lambda} + R\,\mathrm{e}^{\mathrm{i}(\omega_+-\omega_-)t+\mathrm{i}\omega_-\tau'}\frac{\mathrm{d}\omega_-}{\mathrm{d}\lambda}\right)\Big/\Delta, \tag{66}$$

$$C = \mathrm{i}\frac{\mathrm{d}\omega_+}{\mathrm{d}\lambda}\,\frac{R\,\mathrm{e}^{\mathrm{i}\omega_+\tau'-\mathrm{i}\omega_-t} + Q\,\mathrm{e}^{\mathrm{i}\omega_-(\tau'-t)}}{\Delta}, \tag{67}$$

where

$$Q = \frac{1}{\mu}\,\frac{1-\mu}{1-\xi\mu}, \quad R = \xi\left(\frac{1-\mu}{1-\xi\mu}\right)^2, \quad \Delta = 1 - R\,\mathrm{e}^{\mathrm{i}(\omega_+-\omega_-)t},$$

$$\mu = \frac{1}{2n_\mathrm{b}}(2n_\mathrm{b} + 1 + \mathrm{i}\omega_+/\Gamma_\mathrm{b}), \quad \xi = n_\mathrm{b}(1+n_\mathrm{b})^{-1}.$$

After simple integration in eq. (58) over τ we obtain

$$\frac{\mathrm{d}F(t)}{\mathrm{d}\lambda} = \mathrm{i}\frac{\mathrm{d}\omega_+}{\mathrm{d}\lambda}t + \frac{\mathrm{d}}{\mathrm{d}\lambda}\ln\left(\frac{1-\xi\mu^2}{(1-\xi\mu)^2}\,\frac{1}{\Delta}\right), \tag{68}$$

The solution of eq. (68) with the boundary condition has $F(t)|_{\lambda=0} = 0$ the form

$$F(t) = \mathrm{i}(\omega_+ - \mathrm{i}\Gamma_\mathrm{b})t + \ln\left(\frac{1-\xi}{(1-\xi\mu)^2}\,\frac{(1-\xi\mu^2)}{\Delta}\right), \tag{69}$$

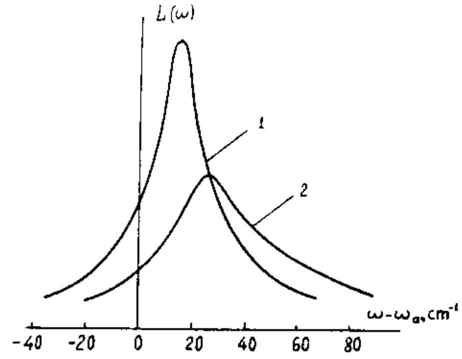

Fig. 4. Temperature dependence of the exchange lineshape for $\delta\omega = 2\Gamma_b = 37$ cm^{-1}, $\omega_b = 220$ cm^{-1}, (1) $T = 200$ K; (2) $T = 300$ K.

where ω_+, μ and Δ are taken at $\lambda = \delta\omega$. The lineshape is given by

$$L(\omega) = -\operatorname{Im}(1-\xi)\frac{1-\xi\mu^2}{(1-\xi\mu)^2}\sum_{n=0}^{\infty}\frac{R^n}{\omega-\omega_a-\Delta\omega_n+i\Gamma_n}, \tag{70}$$

where

$$\Delta\omega_n = -\operatorname{Re}[\omega_+ + n(\omega_+ - \omega_-)],$$
$$\Gamma_n = +\operatorname{Im}[\omega_+ + n(\omega_+ - \omega_-)] - \Gamma_b.$$

From formula (70) it is easy to obtain the limiting formulas which were considered previously by other authors [9–12]. Independently formula (70) was obtained recently by Makarov and Tyakht [18] who used a reduced density matrix technique within the constraints of a Markoff approximation. Thus the validity conditions of a Markoff approximation for the exchange model are equivalent to the requirement that the local phonon Green's function can be written in the form (61).

The temperature dependence of the lineshape is shown in fig. 4. The parameters chosen for $\delta\omega$, $\eta = 2\Gamma_b$ and ω_b ($\delta\omega = \eta = 37$ cm^{-1}, $\omega_b = 220$ cm^{-1}) are expected for the C–O stretching vibration mode for a CO molecule adsorbed on Cu(100) [9]. The calculated lineshape clearly show an asymmetry on the high-energy side of the resonant frequency. This asymmetry is increasing with raising temperature.

4.2. Cubic anharmonism

Let us now consider the exchange model with a cubic anharmonism when

$$H_{ab} = \delta\omega a^+ a(b^+ + b). \tag{71}$$

In this case $S(t)$ is the transient response of substrate phonons to the abrupt change of the force acting on the mode B. This response function is determined by the well-known results (see for example ref. [19]). From this results one can easily obtain

$$S(t)=\mathrm{e}^{-g(0)+g(t)+\mathrm{i}\,\Delta\omega t}, \tag{72}$$

where

$$g(t)=\left(\frac{\delta\omega}{\omega_\mathrm{b}}\right)^2\left[(1+n_\mathrm{b})\,\mathrm{e}^{-\mathrm{i}\omega_\mathrm{b}\tau-\Gamma_\mathrm{b}|\tau|}+n_\mathrm{b}\,\mathrm{e}^{\mathrm{i}\omega_\mathrm{b}\tau-\Gamma_\mathrm{b}|\tau|}\right]$$

$\Delta\omega=(\delta\omega)^2/\omega_\mathrm{b}$ is the constant frequency shift which will be further omitted. The lineshape is given by

$$L(\omega)=\mathrm{Re}\,\mathrm{e}^{-g(0)}\int_0^\infty \mathrm{e}^{\mathrm{i}(\omega-\omega_\mathrm{a})t}\,\mathrm{e}^{g(t)-\gamma t}, \tag{73}$$

where we introduce the damping constant γ due to the terms of the Hamiltonian which are not taken into account in the present exchange model. After expanding $\exp(g(t))$ in powers of $g(t)$ we obtain

$$L(\omega)=\mathrm{e}^{-g(0)}\sum_{n,m=0}^{\infty}\frac{(1+n_\mathrm{b})^m}{m!}\frac{n_\mathrm{b}^n}{n!}\left(\frac{\delta\omega}{\omega_\mathrm{b}}\right)^{2(m+n)} \times\frac{\gamma+(m+n)\Gamma_\mathrm{b}}{(\omega-\omega_\mathrm{a}-(m-n)\omega_\mathrm{b})^2+(\gamma+(m+n)\Gamma_\mathrm{b})^2}. \tag{74}$$

Each term in (74) corresponds to the transition 0 → 1 between the ground and the first level of mode A which is accompanied by creation of m and annihilation of n phonons of the low frequency mode B. In the limit of low temperature the contribution from the term with $n=1, 2, \ldots$ can be neglected. In this case we have

$$L(\omega)=\mathrm{e}^{-g(0)}\sum_{m=0}^{\infty}\frac{(1+n_\mathrm{b})^m}{m!}\left(\frac{\delta\omega}{\omega_\mathrm{b}}\right)^{2m}\frac{\gamma+m\Gamma_\mathrm{b}}{(\omega-\omega_\mathrm{a}-m\omega_\mathrm{b})^2+(\gamma+m\Gamma_\mathrm{b})^2} \tag{75}$$

Thus a cubic term produces satellites at $\omega_\mathrm{a}\pm\omega_\mathrm{b}$, $\omega_\mathrm{a}\pm2\omega_\mathrm{b}$, … . Taking the strength of the central peak to be unity, the strength at $\omega_\mathrm{a}\pm\omega_\mathrm{b}$ can easily be obtained as

$$f_\pm=\left(\frac{\delta\omega}{\omega_\mathrm{b}}\right)^2\left(n_\mathrm{b}+\frac{1\pm1}{2}\right)\frac{\gamma}{\gamma+\Gamma_\mathrm{b}}. \tag{76}$$

For estimation we can describe the interaction between the adatom and the nearest substrate atom by a Morse potential [13]. In this case it may be shown that

$$f_\pm=\frac{9}{16}\left(\frac{m_\mathrm{a}}{m_\mathrm{b}}\right)\left(\frac{\omega_\mathrm{a}}{\omega_\mathrm{b}}\right)^3\left(\frac{\omega_\mathrm{a}}{D}\right)\left(n_\mathrm{b}+\frac{1\pm1}{2}\right)\frac{\gamma}{\gamma+\Gamma_\mathrm{b}}, \tag{77}$$

where m_a is the adatom mass, m_b is a mass of the substrate atom. D is the adsorption energy. For $\gamma \gg \Gamma_b$ formula (77) coincides with the perturbation theory result [13]. However, usually $\gamma \ll \Gamma_b$. For vibration of CO on Ni(100) $\omega_a = 480$ cm^{-1}, $\omega_b \simeq 150$ cm^{-1}, $D = 1 \times 10^4$ cm^{-1}, $\gamma = 15$ cm^{-1}, and $\Gamma_b \simeq 40$ cm^{-1} [13]. The use of these number in (77) at room temperature gives sidebands of $\simeq 15\%$ strength. Perhaps this could be seen experimentally.

In our consideration we neglected the cubic terms $a^+a^+\varphi$ and $aa\varphi$ in the interaction Hamiltonian. As it was pointed by Langreth et al. [13] this terms make a contribution to the pure-dephasing linewidth arising by going to fourth-order perturbation theory which is roughly equal to the contribution made by the quartic term. Such a contribution is due to second-order processes which are related to creation of the virtual vibrational state of the adsorbate off the mass shell. Therefore detecting sidebands would verify the presence of the phonon-dephasing mechanism [13].

At high temperature we may evaluate lineshape (73) by a saddle point method to obtain

$$L(\omega) = \frac{1}{\delta\omega}\sqrt{\frac{\pi}{n_b}}\exp\left(-\frac{(\omega-\omega_a)^2}{2(\delta\omega)^2 n_b}\right). \tag{78}$$

Thus in the high temperature limit the lineshape is a Gaussian with a full width at half maximum given by

$$\Gamma_a = 2\delta\omega\sqrt{2\ln 2 n_b} \sim \sqrt{T}. \tag{79}$$

5. Conclusion

In the interpretation of the measured lineshapes of the vibrational modes of adsorbates on a surface a careful analysis of different broadening mechanism is necessary both theoretically and experimentally.

In this paper our aim was to present a theoretical analysis of the lineshape due to energy and phase relaxation. It was shown that for vibration parallel to the surface the presence of the electron–hole pair damping mechanism necessarily produces an asymmetric lineshape just as in the case of vibration normal to the surface. The observed asymmetric lineshape of the overtone infrared adsorption of the wagging mode of H on W(100) may be considered as the evidence for electron–hole pair coupling of an adsorbate vibration on a metal substrate. In the presence of electron–hole pair mechanism of line broadening the dephasing width is always negligible in comparison with the lifetime width. The dephasing contribution to the linewidth due to elastic scattering of electrons in fourth-order processes seems to be more important in comparison with elastic electron–hole pair scattering.

The exchange model of phase relaxation with a quartic and cubic anharmonism is studied. In both cases the vibrational line profile is obtained exactly and analytically. A quartic as well as cubic term not only gives a dephasing contribution to the central peak of frequency ω_a but also produces satellites peaks. For a quartic anharmonism the contribution from satellites can be neglected in many cases. The different temperature dependence of the frequency shift and the linewidth can be used to distinguish between the different cases (cubic and quartic anharmonism) and therefore also, at least in principle, to derive information about bonding site symmetry.

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